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Preface

When this project started I had worked at Cementa Research for nine years after studies of chemistry at Stockholm University and two years of doctoral studies in aquatic chemistry. At Cementa Research I have worked with analysis and investigations on cement and raw materials for cement manufacturing, and with quality improvements using statistical methods. Before the start of my present doctoral studies, I was thus well oriented about cement manufacturing and cement hydration.

This doctoral work was an opportunity for me for personal development and to gain more knowledge about cement and concrete. During the years this project has been running we have started a new field within Cementa Research. Organic analysis used to mainly be made by the FTIR technique. Now we have two gas chromatographs with different injection and detection systems. Parallel to this project climate rooms have been built and equipment for emission measurements has been bought and installed. Development of methods on the new instruments and measuring procedures on the sampling equipments has been made both in this doctoral work and also in response to the needs of Cementa Research's customers. Since this is a rather new area we have spent a lot of effort to get functional equipment and to develop methods and procedures, some of which are reported in this licentiate thesis.

This doctoral project has been made at the Division of Building Materials at Lund Institute of Technology (LTH) and it has also been a part of the industrial research school, "The Building and Its Indoor Environment" at Lund University.

For the funding of this project Cementa, Norcem, Abetong, Betongindustri and KK-stiftelsen are gratefully acknowledged.
I am also very grateful to Cementa Research for giving me the opportunity to perform these studies. I also send many thanks to Åsa Nilsson, Cementa, and Paul Sandberg, W R Grace, for giving me advice and information about cement and admixtures.

My colleagues at Cementa Research are gratefully acknowledged for both technical help and encouraging me during my work.

Thanks to the people at the Building Materials at Lund Institute of Technology for being a second family for me when I attended the courses at LTH. Special thanks to my supervisors, Göran Fagerlund, for giving me an understanding of the material concrete, and to Lars Wadsö, that with an enormous portion of patience has guided me all the way through this work.

Last but not least I will thank my family, especially my children that have had to stand the circumstances with a travelling mother.

Summary

This work concerns emissions of volatile substances from conrete and methods for measuring emissions from this material (emissions of particles or radioactivity are beyond the scope of this work). KK-stiftelsen, Cementa, Norcem, A-betong and Betongindustri have founded this work.

The major part of this work deals with a new method for quantification of VOCs in concrete. There is a need for this type of quantification due to the development in cement and concrete production using plasticizing agents and fillers for improved rheological properties, and alternative fuels and waste materials to reduce the environmental impact of cement production. Measurements are needed to show that these actions do not influence the emissions from the products. Quantification by using multiple headspace extraction gas chromatography (MHE GC) is a fast and simple method. The samples are prepared of crushed concrete, put in sealed vials and repeated measurements are performed by incubation in temperatures above 100°C for 45 minutes and headspace gas are extracted from the vial into the gas chromatograph for separation and detection of the VOCs. The method is calibrated by measuring known amounts of VOCs added to empty vials. This work is reported in the first paper and then continued in the second paper appended to the thesis. The method works for the alcohols, n-propanol, n-butanol, n-hexanol and 2-ethyl-1-hexanol, and for some more high boiling alkanes, as pentadecane and octadecane. We have not been able to show that it works for low boiling alkanes, since they probably are lost from the sample before the analysis. Other high boiling and polar compounds seem to be too strongly adsorbed for quantification with this method.

The second study (appended as the third paper), deals with ammonia emissions from cement ground with different grinding aids. Ammonia emissions are measured from the ground cement and mortars made of the ground cements. The cements were ground of clinker, limestone, slag, gypsum, and iron sulphate and different grinding aids in the same proportions used for production of the Swedish cement, called "Byggcement". Five different grinding aids were tested, of which four contained nitrogen in the amine-form.

One of the grinding aids gave rise to quite high early ammonia emissions, both from cement powder and from mortar. When the ammonia emissions were measured after 8 days from cement and 14 days from mortar the emissions had decreased to low values. There were also ammonia emissions from the cements ground without grinding aid and with grinding aid without nitrogen showing that other components in the cements contained nitrogen in an amine-form. Measurements showed that there were ammonia-forming nitrogen compounds in the limestone, the slag and also in the clinker.

A result of these studies is the knowledge of the importance of the choice of methods used for emission measurements. When one measure emission rates, as is the common procedure for building materials both for primary and secondary emissions one should be aware of that the emission rate is influenced by the transport of the VOCs in the material. With a material like mortar or concrete you have to consider what porosity you have, where you are on the desiccation curve and the solubility in water of the VOCs you are interested in. If you are interested in the potential of emissions in the material a quantification of the adsorbed VOCs is a useful complement to emission rate measurements.

Sammanfattning

Det här projektet gäller emissioner av flyktiga föreningar från betong och metoder för emissionsmätningar på dessa material (emissioner av partiklar och radioaktivitet behandlas inte i detta arbete). KK-stiftelsen, Cementa, Norcem, A-betong och Betogindustri har finansierat detta arbete.

Den större delen av arbetet har ägnats åt en ny metod att kvantifiera flyktiga organiska föreningar (VOC) i betong. Det finns ett behov av denna kvantifiering på grund av utvecklingen inom cement- och betongproduktionen med större användning av flyttillsatser och filler för förbättrade reologiska egenskaper och användning av alternativa bränslen och avfall för att reducera miljöpåverkan vid cement- och betongproduktion.

Det behövs mätningar för att visa att dessa förändringar inte påverkar emissioner till innemiljön från produkterna. Kvantifiering med hjälp av upprepade headspace extraktioner och gaskromatografi (MHE GC) är en snabb och enkel metod. Proven från betong krossas och sätts i vialer som försluts tätt. Upprepade mätningar görs med inkubering (behandling) i temperaturer över 100°C under 45 minuter. Därefter tas gasprov från vialen och injiceras i gaskromatografen, där föreningarna separeras och detekteras. Metoden kalibreras genom analyser på kända halter av VOC-er i tomma vialer. Det här arbetet är beskrivet i första artikeln och en fortsättning av arbetet är beskrivet i den andra bifogade rapporten. Metoden fungerar för alkoholerna, n-propanol, n-butanol, n-hexanol och 2-etyl-1-hexanol, och för några högkokande alkaner, som pentadekan och oktadekan. Vi har däremot inte kunnat visa att den fungerar för lågkokande alkaner, för de har förmodligen förångats från provet redan före analysen.

Andra högkokande polära föreningar verkar vara för hårt absorberade för att kunna kvantifieras med vår metod.

Den andra studien (bilaga 3) behandlar ammoniakemissioner från cement malda med olika malhjälpmedel. Mätningar har gjorts av ammoniakemissioner från de malda cementen och från bruk gjorda på dessa cement. Cementen maldes av klinker, kalksten, slagg, gips och järnsulfat och olika malhjälpmedel i motsvarande mängder som används vid produktionen av ett svenskt cement som heter Byggcement. Fem olika malhjälpmedel testades av vilka fyra innehåller kväve i amin-form.

Ett av malhjälpmedlen gav upphov till ganska hög, tidig ammoniakemission, både från cement-pulvret och från bruket. När ammoniakemissionen uppmättes efter 8 dagar på cementen och efter 14 dagar från bruken hade den sjunkit till låga värden. Det var också mätbara nivåer av ammoniak från cementet utan malhjälpmedel och från cementet med malhjälpmedel utan kväve, vilket visar att andra komponenter i cementen innehöll kväve i amin-form. Analyser av kalkstenen, slaggen och även klinkern visade att de innehöll kväve i någon form som kunde bilda ammoniak i analysen.

Ett resultat av dessa studier är kunskap om betydelsen av valet av vilken metod som används för emissionsmätningar. När man mäter emissionshastigheter, vilket är det normala för byggnadsmaterial både vid mätningar av primära och sekundära emissioner, ska man vara medveten om att emissionshastigheten påverkas av transporten av VOC-er i materialet. Om det är ett material som bruk eller betong måste man ta i beaktande vilken porositet man har, när i uttorkningsskedet man provtar och hur vattenlösliga de föreningar man studerar är. Om man behöver bedöma vilka potentiella emissioner det finns i ett material är en kvantifiering av innehållet ett bra komplement till mätningar av emissionshastighet.

List of appended papers

Multiple Headspace Extraction Gas Chromatography for Quantification of VOCs in Concrete. Hjellström, T, Wadsö, L and Kristensen, J (2002). Proceedings from the 9th International Conference on Indoor Air and Climate, Vol. 2 pp. 914-919. Monterey, CA, USA.

Multiple Headspace Extraction Gas Chromatography Quantification of Eleven Volatile Organic Compounds in Concrete. Hjellström, T, Wadsö, L and Kristenson, J (2003) not submitted yet.

Emission of Ammonia from Cement Ground with Different Grinding Aids. Hjellström, T and Wadsö, L (2003). not submitted yet.

Contents

1. Introduction

1.1 Background

The interest in the quality of our indoor environments has for the last thirty years been steadily increasing. One issue that is important today is the indoor air quality. We know that materials and activities in a building can produce unwanted odours and unhealthy substances. We also know that moisture is a key issue concerning the indoor air quality as reactions in materials producing secondary emissions are much more likely to occur when the humidity is raised. We also know that there are connections between moisture/humidity and health (Bornehag, et al, 2001), although these relations are very difficult to delineate.

As the interest in indoor air quality has increased, the interest in methods to be used to investigate indoor environments have also increased. Researchers and consultants now have a rather large battery of methods for studying both indoor air quality and health, e.g. VOC sampling and analysis methods for volatile organic compounds (VOC), questionnaires, and quantitative measures of mucous membrane irritation.

In this work I have investigated two indoor air quality aspects of concrete as a construction material:

- The possible emission of ammonia
- Methods to quantify adsorbed VOCs in concrete.

1.2 Aim of the thesis

The aim of this project is to see how concrete performs concerning chemical emissions to the indoor environment. This concerns both the primary and the secondary emissions. Primary emissions are substances that are present in the concrete from its production. Their emissions usually decrease with time, but the rate at which they are emitted is dependent on many factors, e.g. the desiccation rate of the concrete and its porosity. Secondary emission is the emission of substances formed in the material from reactions between substances or degrading processes or release of adsorbed substances from earlier activities. A special case of secondary emissions is the re-emissions of substances adsorbed by a material. We do not know of any substances added during production that degrades in concrete, but polymeric materials in contact with concrete can produce large amounts of secondary emissions under unfavourable conditions. A common Swedish example is the degradation of flooring adhesives on humid concrete. As concrete has a high adsorption capacity (it is a very porous material with a large internal surface) it can absorb these secondary emissions, and later re-emit them into the indoor environment (e.g. if a tight flooring is replaced by a permeable flooring).

1.3 Limitations

The materials and methods used in the construction industry vary considerably from country to country, and region to region, e.g. in Sweden we use much less filler materials in our cements than one does in many other countries. In this project we have mainly worked with materials and methods used in the Nordic countries. We have, however, also tried to make reference to international literature whenever possible.

In this project we have concentrated on emissions of ammonia and VOC from concrete. Other emissions, e.g. of radioactive radon gas, are outside the scope of this project.

1.4 Disposition of the thesis

In this thesis the studies are reported in three papers which are appended at the end. Two of them concerns the multiple headspace extraction gas chromatography method for quantification of VOCs in concrete and the third is about ammonia emissions from cement ground with different grinding aids.

In chapter 2 a short description of the production path of cement is given as a background for the discussion of possible emission that is following in chapter 3. In that chapter both primary and secondary emissions are discussed, with the focus on primary emissions. In chapter 4 there are a discussion about methods used for measuring emissions of volatile compounds from and in concrete. This is a central part of the thesis, since methods that were developed for surface materials in indoor environments may not be suitable for mineral-based, hydration products. Chapter 5 gives summaries of the three papers. Chapter 6 gives general conclusions and in chapter 7 future investigations in this field are discussed.

2. From the quarry to the building

It is relevant to give a summary of cement and concrete production as a background for the discussion of possible sources of volatile compounds. To start with the cement production the first step is the blasting of limestone in the quarry. Then the limestone is milled together with sand and iron oxide to a raw meal. Then follows preheating and calcination in a series of cyclones, before the raw meal enters the kiln. There it is burnt in an oxidizing atmosphere. After reaching a temperature of 1500°C, the half-melted material is cooled by fresh air. The solidified lumps are called clinker and these are crushed before transport to the storage.

The final step in the cement production is the milling, where clinker, limestone, gypsum and slag are milled together. A small amount of iron sulphate is also added and grinding aid is used to improve the milling and the handling of the dry cement powder. The cement is stored in silos or directly packed in bags. Cement produced from limestone-rich clinker and without filler is called Portland cement. The term *cement* may also be used for other mineral powders that react with water to form solids, e.g. aluminate cements. However, most cements used in the construction industry contain 30-100% Portland cement.

When water is added to the cement powder, the cement will hydrate and form a solid called hydrated cement paste. The hydration reactions are rather complex and not well known in all details (Taylor 1997). As a first step initial dissolution of ions from the cement grains take place together with initial reactions. Then follows a long (several hours) dormant period during which the cement paste is still fluid after which the main hydration reactions take place over a long time period. Normally the maximum reaction rate takes place after about 10 hours, but the hydration reactions will continue for years, albeit more and more slowly. The formed hardened cement paste is a nano-porous material with very high surface area, typically 200 m^2/kg (Fagerlund 1994).

In concrete production, cement, water and aggregates like sand, gravel and crushed stone are used. The major part of a concrete is the aggregates; the hardened cement paste acts as an adhesive holding the aggregates together. Sometimes also fillers (additives) like silica, limestone or fly ash are added. Today all concrete also contains admixtures like plasticizers, accelerators, retarders and anti-freeze agents, depending on the type of concrete and the time of the year.

The most important parameter in concrete production is the water-cement ratio (the mass of water divided by the mass of cement) as this determines the strength and durability of the concrete. A low water-cement ratio gives a stronger and less permeable concrete that generally is of higher quality.

A normal water-cement ratio used in non-critical components in buildings is 0.65; high performance concretes have water-cement ratios in the order of 0.35. However, such low water-cement concretes are generally more expensive and sometimes more difficult to use on the production site.

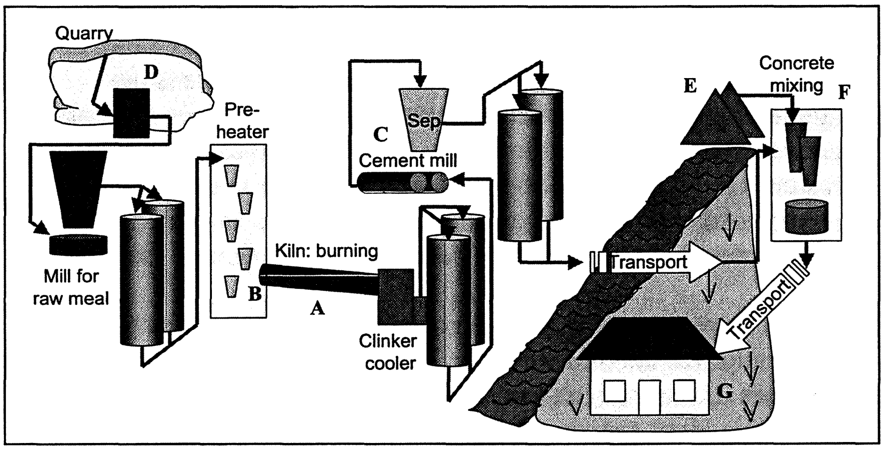

Figure 1. The production path from limestone to building from an indoor air perspective is shown. The most probable sources of VOCs, ammonia and formaldehyde are grinding aids, fillers and reacted gypsum used in the cement mill (**C**), additives and fillers used in the concrete manufacturing (**F**) and form oil used at casting (**G**).

3. Overview of possible emissions

3.1. *Primary emissions*

What possible emissions can there be from concrete? Looking upon the cement and the manufacturing process there cannot be much organic material left in the material after the burning in the kiln (A in figure 1). There are possible sources of ammonium from limestone where potassium may have been exchanged by ammonium in silicate phases (Waltisberg 1988). In the limestone there may also be residues of the nitrogen-containing explosives used in the quarry (D). All those substances and other organic substances will normally be oxidized at the high temperature in the burning zone in the kiln. It has been proposed that there can be partly reducing atmosphere in the kiln by having the burner directed to the material bedding (Peterson 1992). However, this is not likely as the produced cement then will be of low quality.

It is more likely that substances added during grinding will stay in the material. During grinding (C) of cement the temperature rises to about 120°C and the environment is very humid because water is sprayed into the mill to decrease the temperature (otherwise, the high energy input to the mill would heat the cement powder to much higher temperatures at which the gypsum will be dehydrated and not giving the wanted setting conditions). Generally grinding aids are used in the cement mill. The amounts of grinding aid use to be 0.02–0.05 %. They are organic substances, often amine based. This could be a source of ammonia. In Portland-composite cements (CEN 197) up to 35% fillers are used. The fillers can be limestone, slag, burnt shale, pozzolanic materials and fly ash etc. These fillers can be sources of ammonia or sulphides. Presently, in Sweden no other composite cements than limestone-composite cements are produced.

When ammonia is used for NO_x reduction in heat production plants excess of ammonia will end up in the fly ash (Koch and Prenzel 1989; Spanka and Thielen 1999a; Spanka and Thielen 1999b; Rathbone and Tyra 2002). Spanka and Thielen (1999b) show that fly ashes could contain between 8 and 130 mg ammonia/kg fly ash. From concrete with 20% fly ash about 30% of the ammonia content was emitted within 6 days. Similarly, the gypsum from limestone slurries used for gas cleaning of sulphur can also be a source of ammonia. To conclude, there are some potential sources of amines and ammonium compounds in cement that possibly may give rise to ammonia emissions.

It is quite improbable that there are any significant VOC sources in cement. Grinding aids are the only organic compounds used in cement manufacture (except the fuels) and these will mainly give ammonia and low molecular mass volatile alcohols if they break down.

In concrete manufacture (F in figure 1) several different organic additives are used that can theoretically be emission sources. These additives are used in the range of 0 to 2.5% of the weight of cement (usually not more than 1%).

The following is a list of the most common additives in concrete and for what purpose they are used:

- Water reducing agents decreases the friction between particles and makes it possible to decrease the water content by up to 15%. Lignosulphonates are the most commonly used compounds in water reducing agents.

- Plasticizers are used to make concrete more fluid and are useful for reducing the water content for flowing concretes. Both sulphonated melamine formaldehyde or sulphonated naphthalene formaldehyde resin work as plasticizers. These type of plasticizers are often used in high performance concrete. In recent years plasticizers based on polycarboxylates or polycarboxylate ethers are utilised in concretes, both in ordinary concretes and in selfcompacting concretes. These new plasticizers are three times more efficient than the traditional plasticizers.
- Air void agents are used for increased frost resistance of the hardened concrete, sometimes also for stabilizing the concrete by reducing separation. Tall oil (derivates) from pine, alkyl benzene sulphonate and nonyl phenol ethoxylate ester vinsol resin are used as air void agents.
- Calcium formiate and triehanolamine are used as accelerators, that make the hardening reactions going faster.
- Retarders work both by delaying the binding of the cement and by slowing down the reactions resulting in lower heat production in a construction. As retarding agents lignosulphonate compounds, hydroxycarboxylic acids and sugar compounds are used.

There are reports about plasticizers that contain small quantities of volatile organic substances such as formaldehyde, methanol, acetone and ethyl acetate and emissions of some of these volatiles may occur shortly after casting of concrete. Spanka and Thielen (1999b) states that super plasticizers may contain up to 0.6% free formaldehyde. About 30% of the free formaldehyde was released during the first 7 days after casting. After the first week the emissions had decreased to quantities below what was measurable. It is also possible that formaldehyde in strongly alkaline pore solution reacts by the Cannizzaro reaction and forms formic acid and methanol (Spanka and Thielen 1999b).

Another possibly more important source of VOC emissions is the form oil that often is used when concrete is cast in forms. Part of the used oil ends up on interior surfaces of buildings and, depending of the quality of the oil used, may give rise to some emissions. In a Canadian study by Budac (1998) reports high VOC emissions from two different form oils, one mineral based and one based on vegetable oils.

Rock aggregates (E in figure 1) may be contaminated by blasting aids and may by that be a source of ammonia. Other aggregates, e.g. recycled concrete or waste materials, may also possibly contain VOC or VOC-sources.

3.2. Secondary emissions

Secondary emissions originate either from decomposition of substances in a material or from desorption of previously adsorbed compounds. Compounds may break down, e.g. by hydrolysis or oxidization, if the environment is unfavourable, e.g. high temperature, low or high pH, high moisture content, etc. It should especially be noted that many reactions need water or an aqueous solution as reaction media.

In cement based building materials the critical level for solution of compounds and reaction in liquid phase, seems to be above 80% relative humidity (RH) as one rarely seems to get such problems below 85% RH (Saarela 1999) or 83% (Gustafsson 1996). Some examples of reactions giving rise to secondary emissions in cement based materials are:

- The hydrolysis of the polymers of flooring adhesives in contact with humid concrete (Sjöberg 2001). 1-butanol and 2-ethyl-1-hexanol are common emissions. Both these compounds are volatile and odorous and are often found in buildings with indoor air quality problems.

- The decomposition of phthalates used as plasticizers in PVC-floorings (Gustafsson 1996). If there are enough moisture making an alkaline solution in the concrete pores, hydrolysis of the often used di-octylphthalate gives mono-octylphthalate and 2-ethyl-1-hexanol. The first two compounds are considered to have toxic effects (Hideharu 1985; Teirlynck and Rosseel 1985).

It should be noted that critical RH-levels for mould growth seems to be lower than those for chemical degradation. Mould can grow on building materials down to about 70% RH under otherwise favourable conditions. Mould is sensitive to the very high pH of fresh concrete, but as concrete surfaces rather quickly carbonate to get lower pH, surface mould growth is possible on cementitious materials if there is enough moisture, high enough temperature, oxygen and nutrients.

Secondary emissions due to adsorption are an important issue when dealing with a porous material as concrete. The interior surface of concrete is very large and hydrophilic. That means that water and polar organic compounds can diffuse into the material (in both the gas phase and the liquid phase) will be adsorbed in the material. Recently ((Sjöberg 2001; Schoeps et al. 2003) there have been several measurements of VOC-profiles in concrete floors, both showing the typical diffusion profile and that large amounts of volatile substances can be stored in concrete. Figure 2 shows such profiles in concrete floors of buildings.

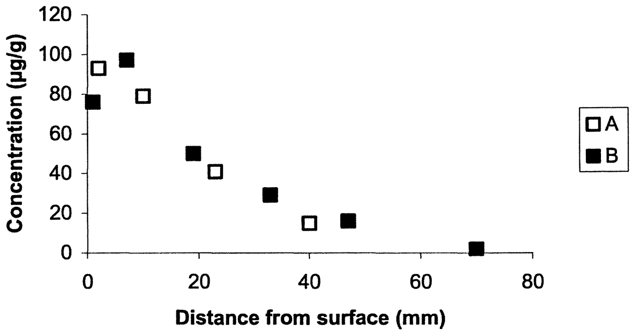

Figure 2. Measured 2-ethyl-1-hexanol profiles in two concrete floors (adapted from (Schoeps et al. 2003)).

4. Emission measurements

Two types of methods exist for studies of volatile compounds and cement based materials. Firstly, methods that measure what comes out of a sample, i.e. what passed through the surface. This is usually termed the *emission rate.* Secondly, methods that quantify the amount of substances adsorbed in a sample, i.e. the *adsorbed VOCs*.

4.1 Measuring emission rates

Measurements of the emissions from different building materials have been made on a relatively large scale for more than ten years now. There are standards for the measuring procedures, e.g Nordtest (1998), Europen Norm (2003a), European Norm (2003b) and European Norm (2003c). The three parts of the CEN-standard concern emission test chamber method (part 1), emission test cell method (part 2) and procedures for sampling, storage of samples and preparation of test specimens (part 3). The results from these methods are the emission rate and it is given as $\mu g/(m^2*h)$. This is also what is often reported in literature. It is usually seen as reasonable to use these measured emission rates as giving the amount of VOCs that will come out of a material per area and time when the material is in use. With this assumption emission rates have been used as a criterion to choose between materials according to their emission of VOC, formaldehyde and ammonia. Even if there is some merit to this approach one should be aware of that emission rates are dependent on a number of different factors, e.g. humidity and porosity. The variations of diffusion coefficients are reported for oxygen diffusion influenced by the relative humidity in different concretes (Tuutti 1982). It may also be difficult to interpret for thicker materials where the VOCs are adsorbed in the material. For such a complex material as concrete the emission rate will probably also be influenced by such factors as the age of the material (degree of hydration).

The transport of VOCs through a material to the surface depends on the moisture conditions. The VOCs highly soluble in water will be easier transported in moist materials, but the less soluble VOCs will to a greater extent evaporate from the surface.

When these kinds of materials have dried out to a level when the floorings are laid, you cannot tell if there still are evaporable compounds left in the material. If there is a rewetting the emissions may rise again.

It is probable that the VOC transport through a material like concrete will be highly influenced by the porosity and there are a large number of factors that controls the porosity. The water to cement ratio is the most important one, but the dispersing action of water reducers and separation in the wet mortar or concrete are two other important factors. The curing conditions also play a decisive role for the permeability of the cement paste. In other words, it is difficult to make the laboratory tests representative for the real products, since we do not have the same recipe with the same aggregates and we do not have the same mixer. This will influence the emission rate in a way we are not aware of.

Emission rates alone, e.g. as measured with a FLEC, are not enough to project the future emissions from a surface like concrete, even if repeated measurements are made.
It is also necessary to quantify the VOCs stored in the concrete, preferably as a function of depth. Together these two types of measurements may make it possible to predict the future emissions.

4.2 Measuring adsorbed VOCs

Compared to the amount of work done to measure emission rates from cement based building materials (and constructions containing cement based building materials), quite little work has been made to measure the total amounts of adsorbed VOCs Apart from the work that we have done we know of two other Swedish groups that have developed this type of methods.

One work is made as a graduate project at Chalmers and the Swedish Testing and Research Institute (SP) in Borås, Sweden (Åberg and Hjelm 2003). Analyses of 1-butanol, toluene and 2-ethyl-1-hexanol were made by multiple headspace extraction gas chromatography with 1-oktanol as internal standard. The results were compared to emitted amounts absorbed by a fibre using solid phase micro extraction. In the MHE analyses equilibrium was not always reached and a method different from the one proposed by Kolb and Ettre (1997) was used: As they did not get straight lines in the semi log relation between areas against injection number other curve fits were made and the sum of the areas were extrapolated to infinite number of injections, This type of procedure does need some validation as one can get very different sums of infinite series depending on which series (equation) one is using. As the measurements were made on ordinary samples of concrete the total amounts of the VOCs were unknown and no recoveries could be given for the method.

Another method has been developed at Pegasus lab in Uppsala, Sweden and Chalmers (Schoeps et al. 2003). The method has been used for quantifying 1-butanol and 2-ethyl-1-hexanol in concrete. The sample of 10 g was placed in the headspace vial together with 5 ml of a displacer of one part ethanol and nine parts water. The analyses are performed with headspace gas chromatography and mass spectrometry detection. The samples are incubated at 85°C for 30 minutes. One measurement given in the paper (Fig. 2 in this thesis) shows the concentration of 2-ethyl-1-hexanol at different depth in a concrete floor. No recoveries were calculated for this method as measurements were only made on samples from a suspected damaged flooring construction.

5. Summary of appended papers

5.1 Multiple Headspace Extraction Gas Chromatography for Quantification of VOCs in Concrete

This paper was presented at the 9th International Conference of Indoor Air and Climate in Monterey 2002. This reports our first series of measurements to create a method for quantification of VOCs in concrete by using the theory of Multiple Headspace Extraction (Kolb 1997). A mix of six VOCs in methanol was added during the mixing of cement, water and sand and the mortar samples were left to harden in closed glass jars. After one day the mortar were crushed and sieved. The grains were charged into vials and sealed with rubber membranes and aluminum caps. Size fractions 1–2 mm, 2–4 mm and 4–8 mm were charged into different vials.

The VOCs in the organic mix used were heptane, nonane, n-propanol, n-butanol, n-hexanol and 2-ethyl-1-hexanol. They were chosen to represent different boiling points and thereby different volatility and different polarity, which would give them different solubility in water and absorption bond strength. To reach equilibrium for the alcohols in the VOC mix 115°C and 45 minutes were needed in the incubations.

We had problems with "pre-injections" in the gas chromatograph because of the overpressure in the vial. In the incubation and injection procedure an amount of the carrier gas is added to make a known overpressure in the vial. If the pressure in the vial is higher than the pressure of the carrier gas there will be a back-flow during the pressurization, leading to leakage of the VOCs into the column before the real injection. The overpressure in our samples comes from the moisture in the samples.

There is always some moisture in concrete samples from buildings and, as the water cannot be removed during sample preparation without also removing VOCs, this is a problem with all such samples. The higher the temperature at incubation the higher the overpressure will be. As discussed in the second paper the overpressure with concrete/mortar samples will often be close to the overpressure one would get with water in the vials.

Because of the above mentioned problems only a few runs were successful, so that we could calculate the recovery. The recovery-figures showed that the alkanes probably were lost already before the analyses. The alcohols with higher volatility showed lower recovery than those with low volatility. For 2-ethyl-1-hexanol the figure of recovery was above one, showing that there was some problem with the quantification. One should note, however, that the calculated recoveries from 0.46 to 1.14 are all in the correct range. As discussed in the second paper, part of the VOCs may be bound in the cement paste and therefore not be measured.

The conclusion of these test measurements was that it would be possible to use this method if one could deal with the overpressure in the vial at incubation. By cooling the sample, one could decrease the loss of VOCs during sample preparation. Another idea was to use solid phase micro extraction for quantification of the VOCs in the headspace and choose a fibre that does not adsorb water. However, there could be problems with leakage caused by the overpressure.

5.2 Multiple Headspace Extraction Gas Chromatography Quantification of Eleven Volatile Organic Compounds in Concrete.

In this study the work with a method for quantification of VOC in concrete was continued (see 5.1). Improvements of the gas chromatograph with a longer column made it possible to handle higher pressures in the vials. Five more compounds were added in the VOC-solution to broaden the study. It now contained five alkanes, heptane, nonane, undecane, pentadecane and octadecane, the same alcohols as in the first study (n-propanol, n-butanol, n-hexanol and 2-ethyl-1-hexanol) mono-octylphthalate and ortho-aminoacetophenone. For this second study the compounds were diluted in dichloromethane.

This time we cast the mortars without VOCs and used only the 2–4 mm fraction. For most of the measurements the VOC-solution was added to the vials with the crushed and sieved mortar before they were sealed. Measurements were then made a few months after the VOCs were added. Some measurements were also made with the VOC-solution added just before the measurements.
Incubation temperatures were 100, 110, 120 and 130°C and the incubation times were 45 minutes (except for one case when 60 minutes was used).

Multiple headspace extractions were performed and for most samples five extractions were made on each sample. For the lighter alkanes the recoveries were low. They had probably to a high extent leaked out from the vials during three months of storage between preparation and analysis. The recoveries for the high boiling alkanes and the alcohols were about 50% to 70% except for one sample when the VOC-solution was added right before the analysis. Then the recovery was 100%. It is probable that some of the VOCs are so tightly bound in the stored samples that one does not succeed in setting them free during the incubation. This shows that you cannot use an internal standard for calibration, since your added standard will not be that strongly bound as other VOCs in the concrete sample.

Further improvements of the method are needed. One solution could be longer incubation times. There are reports of incubations of several hours (Voice and Kolb 1993; Kolb et al. 1994) used in analysis on soil, which is also a porous material with a large internal surface. Another solution could be to use a displacer. By adding a relatively large amount of some compound you may decrease the bond strength between the VOCs and the sample surface.

5.3 Emission of Ammonia from Cement Ground with Different Grinding Aids

This study concerns the occasionally occurring ammonia odour from fresh ground cement and newly cast concrete. This is not a study of indoor air quality (as the concrete will be several months old when people move into a building), but more of ammonia emissions as a sign of degradable compounds in concrete. Cements were ground in a laboratory mill (50 kg). Six grindings with the same clinker, limestone, slag, gypsum and iron sulphate were made. Five different grinding aids were added and four of them contained nitrogen compounds as amines. One grinding was made without grinding aid.

Early emissions of ammonia were measured from the cements ground with different grinding aids and from mortars made with the different cements. The ammonia emissions were measured by sampling the air above the cement sample or the mortar sample and by adsorption of the ammonia in diluted sulphuric acid and detection by spectrophotometry and ion chromatography. Quantification of nitrogen compounds in the ground cements and the raw materials for the cement grinding were also made.

The early ammonia emissions differed largely between the different cements. One of the amine containing grinding aids gave rise to high early emissions.

From the cements without grinding aid and with grinding aid without amines there was also some ammonia emissions, showing that some of the nitrogen compounds in the raw materials were not stable. After eight days the ammonia emissions from cements had decreased to low values.

Also from the mortars made of the ground cements the early ammonia emissions differed. Again the same amine containing grinding aid gave rise to high ammonia emissions after one day. Also the grinding aid without amine content gave rise to quite high ammonia emission at one day, something that was not expected. From the mortars the conventional emission rate was measured. It is not clear whether these unexpected results occurred due to contamination of the cement in the mill or if it was an effect of different porosity (grinding aids can potentially influence the morphology of the cement paste as they are surface active compounds) and thereby influenced the desiccation. Equilibrated mortar in sealed buckets showed less differences between the samples made of the different cements, showing that the large differences in emission rate could be effects of other factors than the VOC concentrations. After 14 days the emission rates decreased to low levels, indicating that ammonia emissions from concrete should not be an indoor air quality problem.

6. Concluding remarks

Concrete is known to be a low emitting building material since it is based of constituents with low volatility. Still some attention of what is added during grinding of cement and at the mixing of concrete is needed so that one does not use admixtures etc. that give rise to emissions. The two methods described in this work should be useful for such work.

7. Future investigations

The studies presented here raised a number of questions that are interesting subjects for future research. The Multiple Headspace Extraction (MHE) is an interesting method, but needs further validation before it can be used to quantify VOCs in concrete.

- The present studies indicates that strong adsorption of VOCs in the cement paste is a potential problem. MHE measurements should be made with longer incubation times and at different times after the VOC-solutions were added to the sample. It is also possible to explore if it is possible to irreversibly desorb the VOCs by heat treatment in the vial, as has been done with soil samples (Voice and Kolb 1993). This can be done after the sampling, but some time before the MHE measurements.
- We have chosen to work without displacers at rather high temperatures. Other studies indicate that displacers and lower temperatures is also a possible combination. This could potentially also solve the problem with strongly adsorbed VOCs.
- It would be interesting to further develop a MHE technique for the quantification of both VOC and water. Such a method could be quite useful for building related investigations.
- The use of MHE-techniques for determining VOC-profiles in concrete slabs is interesting, but it needs further studies on how one shall take representative samples. As the major part of concrete is rock materials that probably have only low VOC contents, this is a problem. Another problem with sampling is how to ensure that VOCs are not lost from the sample during preparation.

The study of ammonia emissions from cement and mortar showed that the emissions of the studied samples were low, but also raised a number of questions:

- Why do the cement ground without nitrogen containing amines show higher ammonia emissions from mortar than cements ground with amines? We believe that the answer may be found in studies of the possible differences in cement paste morphology caused by the grinding aids.
- Our measurements indicate that almost all raw materials contain some nitrogen. It would be interesting to know where this nitrogen ends up in a concrete. There are also some uncertainties about how well the different methods we used work. Quantification methods for nitrogen in different forms, at least amines, in this quite low concentration range, mg/kg, are needed.

Generally, studies of the effect of different additives and fillers on both early emissions of VOC, ammonia and formaldehyde and of later emissions after curing with raised moisture content are of interest. Curing with relevant ventilation is important. During the first period the ventilation rate should be as during the first period when the newly produced concrete is drying. Thereafter the ventilation rate should be quite low to resemble a real case when a floor is laid on concrete.

8. Acknowledgement

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Paper I

Multiple Headspace Extraction Gas Chromatography for Quantification of VOC's in Concrete

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MULTIPLE HEADSPACE EXTRACTION GAS CHROMATOGRAPHY FOR QUANTIFICATION OF VOC'S IN CONCRETE

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ABSTRACT

Concrete itself is not a source of VOC emissions of any importance. However, humid concrete is very alkaline and may cause degradation of organic materials. Concrete can also adsorb considerable amounts of volatile compounds, e.g. from degrading flooring materials. This together with the present trends in cement and concrete production (alternative fuels, new organic additives, waste materials) has made it interesting to develop rapid methods for quantification of VOCs in concrete. We have tested a multiple headspace extraction gas chromatography method to determine the VOC content of cement bound materials. The total VOC content of a sample may be calculated from repeated headspace injections. The sample incubation time and temperature were optimized for six organic compounds with different boiling points and polarity. The method is tested on samples with known additions of these six organic compounds. The method works well on relatively dry samples, but there are problems with over-pressure in the headspace vial from water vapor in humid samples.

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INTRODUCTION

Concrete is the most common building material worldwide and apart from its use in infra structure like bridges and roads most buildings have constructional parts made from concrete. Basically, concrete is made by mixing cement powder, aggregate (sand and rocks) and water. The cement will react (hydrate) with the water and become a solid material called (hardened) cement paste which is the material cementing the aggregate together into a strong, durable material. A mortar is a concrete with only small size aggregate (sand).

There is a lot of experience of using concrete in dwellings and there are no reports of high long-term VOC emissions from the concrete itself. Concrete is therefore often a preferred material in buildings with high demands on the indoor air quality. Budac (1998) and others have shown that except for initial emissions (when the cement is hardening) concrete has very low emissions. Emissions from concrete constructions are not from the concrete itself, but rather from degradation of unstable organic materials in contact with wet concrete that is very alkaline. A very important issue is therefore the initial drying of housing concrete.

Because of the very large internal area of the cement paste, it can act as an adsorbent. When a flooring material or an adhesive in a concrete construction degrades and emitts VOC, a large fraction of these may be adsorbed by the concrete. Sjöberg (2001) shows that when a PVC-flooring with low VOC-permeability is used, up to 50% of the butanol and 2-ethyl hexanol emitted from degrading flooring adhesive may be adsorbed in the concrete floor.

This may later cause problems with re-emissions from the flooring system. Sjöberg (2001) has also measured profiles of butanol and 2-ethyl hexanol in concrete floors and shown that these compounds can over a ten-year period diffuse up to 7 cm into a floor.

The material concrete is changing. For environmental reasons the cement industry has to lower their release of carbon dioxide and are therefore turning to alternative fuels like oil waste, tires, plastic waste etc. There is also an increased use of waste materials and different kinds of additives (e.g. plasticizers) in the concrete production.
All these changes in the production of cement and concrete can potentially result in unacceptable emissions from concrete. The aim of this project is therefore to develop a rapid method of measuring the VOC content of cement based materials.

This paper concerns measurements with Multiple Headspace Extraction Gas Chromatography (MHE GC). This is a method to quantify Volatile Organic Compounds (VOCs) in liquid or solid samples. The theory and practice of MHE is described in Kolb and Ettre (1997). A MHE GC measurement is made by repeating the following steps:

1. Incubation of the closed vial with the sample for a certain time at a certain temperature until VOC-equilibrium between the sample and the gas phase in attained.
2. Injection of an aliquot of the headspace in the vial into the GC-column.
3. Replacement of injected volume with pure carrier gas.
4. Separation of the injected components in the GC column and detection of them with a detector.

Each time the steps above are repeated, VOCs are removed from the vial and the remaining VOCs are diluted by the added carrier gas. Consequently, the amount of VOCs analyzed will decrease for each HS analysis.

The MHE method relies on the fact that there is a constant partition coefficient that determines the distribution between the solid and the gas phase and that there are no adsorption effects in the system (however, note that knowledge of the value of the partition coefficient is not necessary). As the measured GC peak area of a VOC decreases by a certain constant factor *Q* for each injection it is possible to find the total amount of the VOC in the sample vial by summing the converging infinite series in which each term is *Q* times the previous term (Kolb and Ettre, 1997). A properly made MHS analysis will yield a straight line when the logarithm of the peak area is plotted as a function of the injection number (Fig. 1). As long as a sufficient number of injections are made to determine the slope of the line, the total concentration in the sample can be calculated.

Calibration is made by MHE of standards with known amounts of the VOCs of interest injected into vials with deactivated glass beads. This is known as the Total Volatilization Technique (TVT) as the whole sample is in the gas phase. A multiple headspace extraction measurement series made on such a calibration sample also give a straight line in the diagram (Fig. 1).
The evaluation of a MHE calibration is made in the same way as for a measurement of a sample.

The calibration line (Fig. 1) from a calibration will always have a higher absolute slope than that for a solid sample as the calibration is not made with a partitioning system (all the VOC:s are in the gas phase). Monitoring of influences of instrument parameters on the response is made by daily TVT analyses of a standard liquid solution.

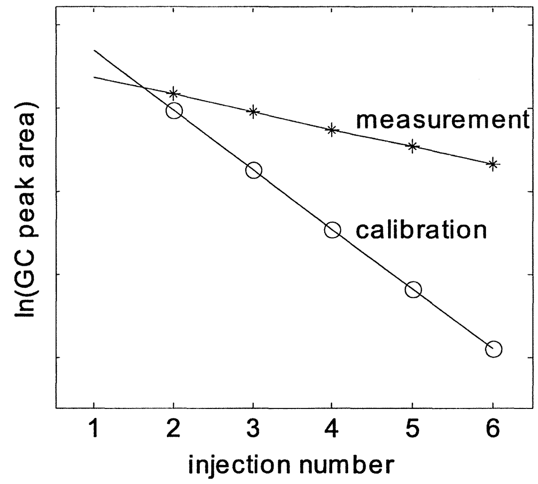

Figure 1. The semilog relationship between peak area and the number of injections (extractions) in MHE measurements of a sample (measurement) and a calibration.

The aim of this method is to quantify the amount of VOCs. To be able to do so it is important to develop a method (sample preparation, incubation time and temperature etc.) that gives equilibrium conditions when the headspace extractions are made. If this is not properly made one will not get straight lines in the semilog diagram and can therefore not evaluate the total concentrations in the samples (Kolb and Ettre 1997).

MATERIALS

To test the method we used mortars made with:

- A Portland cement type II/A-L (EN 197) called ”byggcement” (Cementa AB) produced at a plant in Sweden. It is a cement with less than 15% limestone and not more than 5% slag.
- Fine quartz sand (< 1 mm diameter).
- Potable tap water.

Small mixes of 300g cement, 225g of sand, and 180 g of water were mixed by hand to give samples with a water/cement-ratio of 0.60.The high water/cement ratio will result in a mortar that is porous and with a high relative humidity. For those mixes containing added VOCs (see below), the VOC-mixture was added to the mixed cement and sand just before the water was added.

As the VOC-content of a mortar is very low we added a mixture of VOC with different boiling points and polarity dissolved in methanol. The mixture of organic compounds contained equal amounts (based on molarity, mol/L) of 1-propanol, 1-butanol, 1-hexanol, n-heptane, n-nonane and 2-ethyl-1-hexanol. The alkanes and the alcohols were chosen because of different polarity. Propanol and heptane have boiling points just below 100°C and the boiling points of hexanol and nonane are above 150°C. Butanol and 2-ethyl-1-hexanol are included because they often appear in damaged flooring materials and adhesives and therefore also occur in many studies of indoor air problems. Isothermal calorimetry run on mortar samples with and without the VOC-mix showed that the VOC-mix or the methanol did not change the rate of reaction of the cement mortar.

After about 20 hours hydration at room temperature the mortar was crushed and sieved into different fractions with ASTM sieves. About 5 g of sample particles were weighed into headspace vials and closed with aluminum caps with Teflon coated butyl seals.

The mortar samples were then left to hydrate in the vials. The sample from which results are shown in this paper had a diameter range of 4-8 mm and had been stored at about 22°C for 95 days prior to the measurement.

METHOD

For the MHE GC measurements we used a Perkin-Elmer HS-40 and Autosystem GC with a flame ionization detector. The sample vials were automatically measured with incubation at 110°C for 45 minutes and the GC runtime was 22 minutes. The GC program started at 60°C and ended at 180°C.

RESULTS

Figure 2 shows the semilog relationships from the MHE measurement of a typical sample at 110°C. From the data in this figure we calculated the recovery ratios given in Table 1.

Table 1. Results from a measurement

	1-propanol	1-butanol	1-hexanol	n-heptane	n-nonane	2-ethyl -1-hexanol
VOC in sample	45,4	46,6	43,6	43,2	46,3	46,4
VOC retrieved	20,9	31,5	32,4	3,1	8,8	52,6
Recovery ratio	0,46	0,68	0,74	0,07	0,19	1,14

DISCUSSION

It is seen in Fig. 2 and Table 1 the MHE method has worked satisfactory for most of the compounds. The straight lines with linear regression factors close to one show that equilibrium is reached and quantification is possible for all the compounds.

The recoveries given in Table 1 reflect that volatile compounds were lost during the preparation of the samples. The recovery of the alcohols is relatively high because they have quite low vapor pressures. The figure of recovery for 2-ethyl-1-hexanol is higher one and this probably reflects that the incubation time used for the monitor standard at the date when the sample was analyzed, was only 20 minutes compared to 30 minutes used thereafter. Since 2-ethyl-1-hexanol has the highest boiling point (185°C) of the compounds, it needs the longest incubation time to be vaporized.

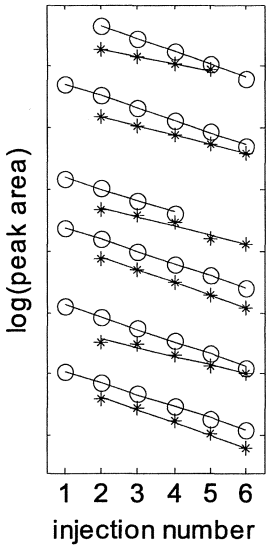

Figure 2. Results from MHE measurements with (from top to bottom): propanol, butanol, heptane, hexanol, nonane, and 2-ethyl-1-hexanol. For each analyzed compound two sets of points are shown: measurements of the sample (asterisks) and measurements of the standard (circles). Note that the result of the first injection is often corrupted and is then not shown.

The alkanes heptane and nonane have low recoveries because they have very low solubility in water and are volatile. During the sample preparation a large fraction of the added amounts of these compounds will evaporate. This is, however, not a problem for the verification of the MHE technique, but is something that has to be considered when samples are prepared for this type of analysis.

Another reason for low recovery of the alkanes may be that they are able to migrate through the Teflon membrane of the vial cups during the long period from the sample preparation to the analysis.

We have had serious problems with using this technique for samples with high moisture content. There are two conflicting factors in the MHE method for solid samples like concrete. One is to make sure that the conditions (sample size, incubation time and incubation temperature) are such that equilibrium is attained. As the materials we are concerned with here have low gas diffusion coefficients and strong adsorption sites, high temperatures are needed to break adsorption forces and to get reasonable equilibration times. However, at high temperatures we will drive off the moisture in the samples and create too high pressures in the vial for the headspace device to work properly. Already at a temperature of 120°C the vial pressure will be too high.

One possible solution to this problem is to use a hydrophobic adsorbent to capture the VOCs, but not the water. One option is the SPME-method (Solid Phase Micro Extraction), in which a small absorbent is introduced in to the vial. However, it is not known if such techniques can be combined with the quantitative MHE-method and if the amounts of VOCs adsorbed on the fiber are enough for quantification. Another hydrophobic adsorbent that could be used is Tenax.

Some other factors that may influence MHE measurements on concrete and mortar are:

- The lower the water content in samples the stronger the VOCs will be bound to the matrix.
- Gas diffusivities are dependent on the pore structure of the cement paste. Generally, samples with low water/cement-ratio have a much tighter structure.

- Samples of concrete contain larger rock aggregate that normally has a very low porosity and will not hold much VOCs. This will give problems for the sample preparation, as GC vials are rather small.
- When samples are crushed and sieved rather large fractions of the more volatile compounds may be lost by evaporation.

We see two uses the type of method we are working with:

1. To investigate concrete constructions that have been exposed to VOCs for long time periods. One example that has recently been investigated in Sweden (Sjöberg, 2001) is n-butanol and 2-ethy-1-hexanol from the degradation of PVC flooring/adhesive laid on concrete. Such information is interesting as it gives an idea of the amounts of VOC that may be re-emitted from such a floor.
2. As a laboratory method for testing for VOC emissions from cementitious materials. It is well known that ordinary Portland concrete is a material with low emissions, but the present trend with an increased use of organic additives, waste and recycled materials in concrete there is a need for new rapid methods to test for emissions.

CONCLUSIONS

We have developed a multiple headspace gas chromatography method that can quantify VOCs in concrete. However, further development is necessary to deal with the problems of over-pressure for moist samples.

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Paper II

Multiple Headspace Extraction Gas Chromatography Quantification of Eleven Volatile Organic Compounds in Concrete

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ABSTRACT

Concrete itself is not a source of VOC emissions of any importance. However, humid concrete is very alkaline and may cause degradation of organic materials and considerable amounts of volatile degradation products can be adsorbed by the concrete material. This together with the present trends in cement and concrete production (alternative fuels, new organic additives, waste materials) has made it interesting to develop rapid methods for quantification of VOCs in concrete. We have tested a multiple headspace extraction gas chromatography method to determine the VOC content adsorbed in cement materials. The total VOC content of a sample may be calculated from repeated headspace injections. The method was tested on samples with known additions of eleven organic compounds with different boiling points and polarity. The method works, as semi quantitative, quite well for the alcohols and alkanes like pentadecane and octadecane, but not for the lighter alkanes.

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Introduction

Concrete is the most common building material worldwide and apart from its use in infra-structure like bridges and roads most buildings have constructional parts made from concrete. Basically, concrete is made by mixing cement powder, aggregate (sand and rocks) and water. The cement will react (hydrate) with the water and become a solid material called (hardened) cement paste which is the material cementing the aggregate together into a strong, durable material. A mortar is a concrete with only small size aggregate (sand). The most important parameter in concrete production is the water-cement (w/c) ratio, the mass of water divided by the mass of cement, used. Traditional concrete has w/c of about 0.6, but in the last decades there has been an increase in low w/c concretes with w/c of about 0.35. When the water-cement ratio of a concrete is decreased the strength will increase and the porosity and permeability will decrease. Low water-cement ratio concrete is therefore in general stronger and more durable, but it is also more expensive.

There is a lot of experience of using concrete in dwellings and there are no reports of high long-term VOC emissions from the concrete itself. Budac (1998) and others have shown that except for initial emissions (when the cement is hardening) concrete has very low VOC emissions. When VOC emissions have been measured from concrete constructions, these emissions do not originate in the concrete itself, but rather from degradation of unstable organic materials in contact with wet concrete that is very alkaline. A very important issue is therefore the initial drying of housing concrete.

Because of the very large internal area of the cement paste, it can act as an adsorbent. When a flooring material or an adhesive in a concrete construction degrades and emits VOC, the concrete may adsorb a large fraction of these. Sjöberg (2001) shows that when a PVC-flooring with low VOC-permeability is bonded with water based adhesive to a wet concrete, up to 50% of the n-butanol and 2-ethyl-1-hexanol emitted from the degrading flooring adhesive may be adsorbed in the concrete floor. This may later cause problems with re-emissions from the flooring system. Sjöberg (2001) has also measured profiles of n-butanol and 2-ethyl-1-hexanol in concrete floors and shown that over a ten-year period these compounds can diffuse up to 7 cm into a concrete slab.

Concrete is a material undergoing large changes today. For environmental reasons the cement industry has to lower their use of fossil fuels and their release of carbon dioxide. They are therefore turning to alternative fuels like oil and plastic waste, tires, etc. and increasing their use of waste materials and different kinds of additives (e.g. plasticizers) in the concrete production. All these changes in the production of cement and concrete can potentially result in unacceptable emissions from concrete. The aim of this project is therefore to develop a rapid method of measuring the VOC content of cement based materials.

This paper concerns measurements with Multiple Headspace Extraction Gas Chromatography (MHE GC). This is a method to quantify Volatile Organic Compounds (VOCs) in liquid or solid samples. The theory and practice of MHE is described in detail by Kolb and Ettre (1997). A MHE GC measurement is made by repeating the following steps:

1. Incubation of the closed vial with the sample for a certain time at a certain temperature until VOC-equilibrium between the sample and the gas phase is attained.
2. Injection of an aliquot of the headspace in the vial into the GC-column.

3. Replacement of injected volume with pure carrier gas.
4. Separation of the injected components in the GC column and detection of them with a detector.

Each time the steps above are repeated, VOCs are removed from the vial and the added carrier gas dilutes the remaining VOCs. Consequently, the amount of VOCs analysed will decrease for each HS analysis.

The MHE method relies on a constant partition coefficient that determines the distribution of a VOC between the condensed phase and the gas phase, i.e. that there are no adsorption effects in the system (however, note that knowledge of the value of the partition coefficient is not necessary). By using high enough temperature the adsorption effects will be removed. It is also necessary to determine how long incubation time is needed for the system to reach equilibrium. Most MHE studies have been made on liquid systems, e.g. for the analysis of blood alcohol (Brown 1988), and only a few studies on solid systems have been described (Bitz and Doelker1995; Milana et al. 1991; Westendorf 1985; Kolb et al. 1984 and Kolb et al. 1981). Solid systems are generally more difficult to work with as there can be large adsorption effects in the solid material and higher temperatures and longer incubation times are needed to reach equilibrium values. The nano-porous cement mortar materials used in this study are no exception to this.

With a partitioning system the measured GC peak area of a VOC decreases by a certain constant factor *Q* for each injection. It is then possible to find the total amount of the VOC in the sample vial by summing the converging infinite series in which each term is *Q* times the previous term (Kolb and Ettre 1997). A properly made MHE analysis will yield a straight line when the logarithm of the peak area is plotted as a function of the injection number (Fig. 1). As long as a sufficient number of injections are made to determine the slope of the line, the total concentration in the sample can be calculated.

Calibration is made by MHE of standards with known amounts of the VOCs of interest injected into vials with deactivated glass beads. This is known as the Total Volatilization Technique (TVT) as the whole sample is in the gas phase. A multiple headspace extraction measurement series made on such a calibration sample also gives a straight line (Fig. 1). The evaluation of a MHE calibration is made in the same way as for a measurement of a sample. The calibration line (Fig. 1) from a calibration will always have a higher absolute slope than that for a solid sample as the calibration is not made with a partitioning system (all the VOCs are in the gas phase). Monitoring of influences of instrument parameters on the response is made by daily TVT analyses of a standard liquid solution.

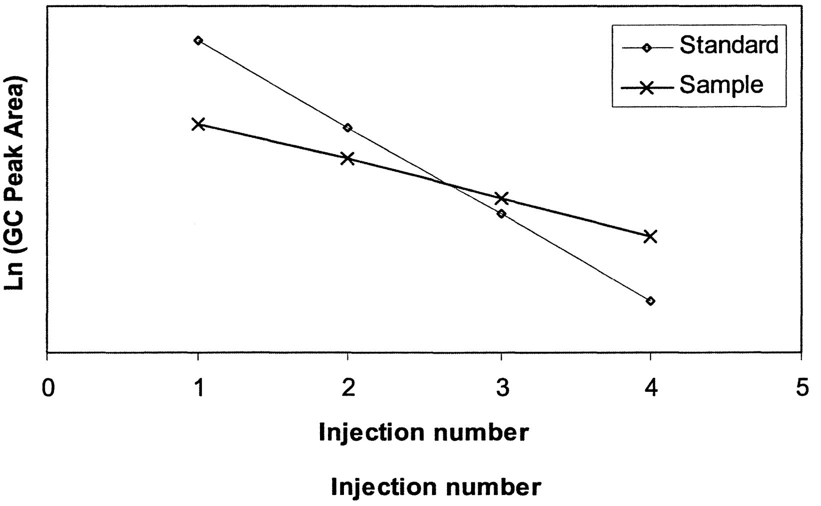


Figure 1. The semi log relationship between peak area and a number of injections (extractions) of a sample and a calibration standard.

The aim of the present MHE-method is to quantify the amount of VOCs in concrete. To be able to do so it is important to develop a method (sample preparation, incubation time and temperature etc.) that gives equilibrium conditions when the headspace extractions are made. If this is not properly made one will not get straight lines in the semi log diagram and the total concentration in the sample cannot be calculated (Kolb and Ettre 1997). It is also important that the slope of the external standard measurements is larger than for the samples, as there should be no partitioning in the standard.

Materials

To test the method we used mortars made with:

- 25% dry weight Portland cement type CEM II/A-L (EN 197) ("Byggcement", Cementa AB, Sweden). It is cement with less than 15% limestone and not more than 5% slag.
- 15% dry weight fine quartz sand (< 1 mm diameter).
- 60% dry weight coarse quartz sand (1 – 2 mm diameter).
- Added potable tap to reach water-cement ratios (mass of water divided by mass of cement) of 0.35 and 0.60.

The dry components were placed in the bowl of a standardized mixer (EN 197-02) and mixed for half a minute before the water was added. After two minutes further mixing the mortar was placed in one-litre sealed glass jars. The mortar was left for hardening in 23°C for 24 hours, and was then crushed and sieved with ASTM sieves. About 5 g of the particle size fraction 2–4 mm was charged into each vial. As the VOC-content of a mortar is very low, different amounts (0.25, 0.45 and 2.0 µl) of an organic solution were added before the vials were sealed with aluminum caps with Teflon coated butyl seals. The mortar samples were then left to hydrate in the vials at about 22°C for 120 to 150 days prior to the measurement. Some plain mortar samples were also stored in vials and measured with VOCs that was added just before the measurement.

The organic solution added contained 11 organic compounds in dichloromethane (see Table 1). The amounts of the components in the vials were about 3 µg, 5 µg or 24 µg for the three different volumes added.

The compounds represent a large range of boiling points. Both non-polar alkanes and polar alcohols were used, as the polar compounds will be more absorbed in the cement materials. N-butanol and 2-ethyl-1-hexanol are included because they often appear in concrete under damaged flooring materials and adhesives and therefore also occur in many studies of indoor air problems. Ortho-aminoacetophenone and mono-octylphthalate are possible decomposition products from plasticizers with suspected health effects (Hideharu 1985; Teirlynck 1985).

Table 1. The organic compounds used.

	Molar weight g/mol	Boiling point °C
N-propanol	60.1	97
N-butanol	74.1	118
N-hexanol	102	158
2-Ethyl-1-hexanol	130	185
Heptane	100	98
Nonane	128	151
Undecane	156	196
Pentadecane	212	271
Octadecane	254	316
O-aminoacetophenone	135	292*)
Mono-octylphthalate	264	248
Dichloromethane	84.9	40

*)O-aminoacetophenone decomposes at 292°C.

Method

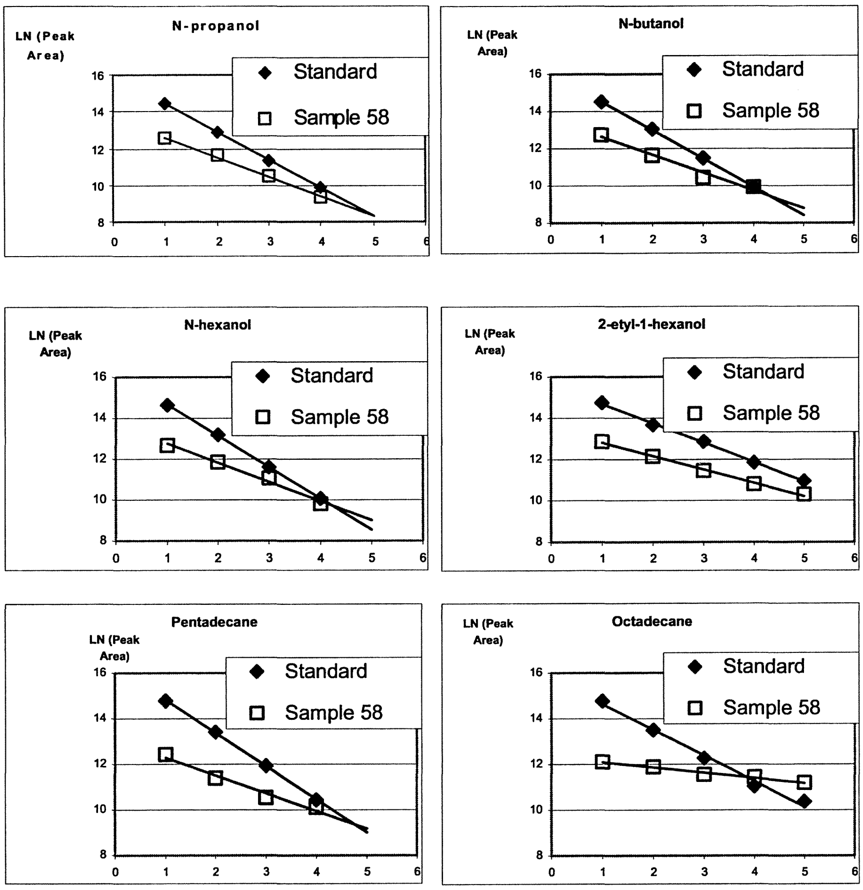
For the MHE GC measurements we used a Perkin-Elmer headspace auto-sampler, HS-40, and gas chromatograph, Autosystem GC, with a flame ionization detector. The sample vials were automatically measured with incubation at 100°C, 110°C, 120°C and 130°C for 45 or 60 minutes. The GC runtime was 22 minutes and the GC program started at 60°C and ended at 180°C.

Results

Figure 2 shows the semi log relationships from the MHE measurement of six compounds in a sample at 100°C. The measurements of the external standards and the sample are used for quantification of the compounds in the sample.

The logarithm of the peak area is plotted for n-propanol, n-butanol, n-hexanol, 2-ethyl-1-hexanol, pentadecane and octadecane against the incubation number, both for the external standard (dark dots) and for a mortar sample with the VOC-mix (empty squares). (Sample 58 corresponds to sample B in Table 2.)

Figure 2.



The results from the quantifications are compared to the amounts added at the sample preparation. The calculated recovery ratios are given in Table 2 together with the regression coefficient as a quality index for the straight lines. The numbers of data points in the lines are also given.
In sample I in Table 2 the organic solution was added just before the incubations.

Table 2. Results from measurements

		Sample A, w/c 0.60		Sample B, w/c 0.35		Sample C, w/c 0.35		Sample D, w/c 0.60		Sample E, w/c 0.60		Sample F, w/c 0.35		Sample G, w/c 0.60		Sample H, w/c 0.35		Sample I***) w/c 0.60	
	Incubation	100°C		100°C		110°C		120°C		120°C		120°C		120°C**)		130°C		120°C	
Heptane	Recovery															2.4%		100%	
	Reg coeff															1.000	2	1.000	4
Nonane	Recovery													6.0%		33%		101%	
	Reg coeff													0.991	3	0.986	3	1.000	4
undekane	Recovery	3.7%		6.2%				9.1%		5.7%								100%	
	Reg coeff	1.000	2	1.000	2			0.995	3	0.914	3							1.000	4
pentadecane	Recovery	27%		28%		34%		86%		44%		36%		11%				104%	
	Reg coeff	0.974	5	0.970	5	0.811	5	0.979	3	0.970	5	0.981	4	0.676	3			1.000	4
oktadecane	Recovery	70%		64%		78%		110%		94%		58%		32%		17%		104%	
	Reg coeff	0.953	5	0.990	5	0.827	5	0.955	3	0.980	5	0.969	5	0.861	4	0.962		0.978	5
n-propanol	Recovery	48%		49%		45%		57%		36%		62%		17%				101%	
	Reg coeff	0.999	4	1.000	4	0.992	4	1.000	3*)	1.000	3*)	1.000	2*)	1.000	2*)			1.000	4
n-butanol	Recovery	48%		47%		49%		72%		42%		63%		19%				101%	
	Reg coeff	1.000	5	0.988	4	0.926	4	1.000	3*)	1.000	3*)	1.000	2*)	1.000	2*)			1.000	4
n-hexanol	Recovery	51%		47%		51%		89%		47%		58%		17%				100%	
	Reg coeff	0.980	4	0.994	4	1.000	2	0.998	3*)	0.997	3*)	1.000	2*)	1.000	2*)			1.000	4

		Sample A, w/c 0.60	Sample B, w/c 0.35	Sample C, w/c 0.35	Sample D, w/c 0.60	Sample E, w/c 0.60	Sample F, w/c 0.35	Sample G, w/c 0.60	Sample H, w/c 0.35	Sample I***) w/c 0.60
	Incubation	100°C	100°C	110°C	120°C	120°C	120°C	120°C**)	130°C	120°C
2-etyl- 1-hexanol	Recovery	55%	48%	57%	109%	49%	59%	23%		97%
	Reg coeff	0.993 5	0.998 5	0.999 3	0.995 3*)	0.982 4*)	0.989 3*)	1.000 2*)	4	1.000 5
o-amino acetophenone	Recovery	340%			73%	82%	65%	190%	21%	94%
	Reg coeff	0.992 5			0.993 3	0.642 5	0.822 5	0.486 5	0.990 3	0.953 5

*) The slope is smaller for the sample than for the standard showing that there is leakage in the system.

**) For sample G the incubation reached for 60 minutes instead of 45 minutes.

***) In sample I the VOC-mixture was added just before the measurement.

DISCUSSION

It is seen in Fig. 2 and Table 2 that the MHE method has worked satisfactory for the alcohols and the high boiling alkanes. The straight lines with linear regression factors close to one show that equilibrium is reached and quantification is possible. Table 2 shows that equilibrium is reached for these compounds at 100°C and 110°C as the regression coefficients are close to one. At 120°C for the alcohols the slopes are higher for the sample than for the standards. According to (Kolb and Ettre 1997) this occurs when there is a leakage at the injection site, but this seems not to be the case here, as the alkanes and ortho-aminoacetophenone do not show the same behaviour.

The lighter alkanes, heptane, nonane and undecane, did not perform well. Presumably, these substances have evaporated from the closed vial during the rather long storage time so the concentrations are too low to be measurable. When the concentrations are low one will just get results from a few incubations and the slope of the lines becomes uncertain. This is aggravated by that the result from the first incubation often is quite uncertain.

The ortho-aminoacetophenone was not possible to quantify, probably because it's low volatility and low stability at high temperature (decomposes at about 290°C). Mono-octylphthalate was not detected. Probably low volatility and strong adsorption made the concentration too low.

Although there are straight lines for the alcohols, pentadecane and octadecane and the relation between standard and sample is correct at least at 100°C and 110°C the recoveries are low for sample A – H that had been stored with the VOCs for 4 – 5 months (Table 2). The recovery for sample I with VOCs added just before the measurement was close to one and the regression lines for standard and sample was parallel showing that there is no partitioning.

One reason for the low recoveries of sample A-H could be that the VOCs migrate through the Teflon membranes of the vial cups during the long period from sample preparation to analyses. It is then probable that the unpolar and more volatile compounds disappear faster than the alcohols and the high boiling compounds.

Another possibility is that the VOCs have migrated to strong absorption sites during the long storage time. Physical adsorption by van der Waals forces is almost fully reversible, but chemical adsorption by electron sharing is much less reversible (Gunnarsen and Kjaer 1999). Also the moisture content will impact the binding possibilities. It is most likely that the alcohols are strongly absorbed in the material. Larger hydrophobic molecules will have a slow diffusion in the pores of the material. VOCs might also be irreversible absorbed in the structure when cement hydrates.

It has been shown that recovery of VOCs from high surface area solids can decrease as time between addition of VOCs and MHE analysis increases. (Kolb et al.1994) and (Voice and Kolb 1993) give examples of low recovery with a particulate solid, ("Fuller's earth") with added volatile aromatic and chlorinated hydrocarbons. When the MHE desorption was carried out after 3 hours the recovery was 91% but after 2 days it was only 21%. To reach the same recovery (91%) after 2 days they had to incubate for 4 hours instead of 1 hour.

The above phenomenon is quite interesting in connection to the determination of VOCs in concrete floors as these VOCs often have had very long times to be absorbed in the cement paste structure. It may then be that very long incubation times or high temperatures are needed for the proper extraction of all VOCs. Another possibility is to use displacers, substances that are added to the sample in rather large amounts before the incubation and that compete with the VOCs for absorption sites. We have tested benzyl alcohol (α-hydroxy toluene) as a displacer with negative results, but other substances can also be used.

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It is probably difficult to successfully measure the more volatile unpolar substances like heptane and nonane in concrete samples from the field, as one is likely to loose a high fraction of them during sample preparation (crushing) unless this is done at very low temperature.
This should not be a problem for the validation of the MHE technique as one then adds the VOC into the sample vial. For the verification it is, however, crucial that the VOCs do not migrate through the septa (seal) during the long storage times one probably should use to get samples with VOCs bound to the matrix in a realistic way. We used rubber-teflon septa, but it may be that rubber aluminium septa are tighter.

When one uses the MHE method one has to make sure that the conditions (sample size, incubation time and incubation temperature) are such that equilibrium is attained. As the materials we are concerned with here have low gas diffusion coefficients and strong absorption sites, high temperatures are needed to break absorption forces and to get reasonable equilibrium times. However, at high temperatures we will also drive off the moisture in the samples and create high pressures in the vial making it more difficult for the headspace device to work properly.

We have made some measurements of the pressure attained inside heated vials with cement mortar. The result was that even in mortars of normal moisture contents the water vapour pressure reaches values close to the saturation vapour pressures at 100, 110 and 120°C. This means that one should always design MHE measurements on cement based materials so that they can handle the saturation pressure of water plus the original atmospheric pressure. For 100, 110 and 120°C the total pressure will be 1.00, 1.46 and 1.96 atm. For the Perkin-Elmer HS 40 used in the present measurements the pressure of the carrier gas has to be raised to 3 atm for incubations at 120°C.

Some other factors that may influence MHE measurements on concrete and mortar are:

- The adsorption of VOCs in hardened cement paste may be dependent on the moisture content. It is probable that polar compounds compete for adsorption sites with water, so that high water contents may drive away VOCs.
- Gas diffusivities are dependent on the pore structure of the cement paste. Generally, samples with low water-cement ratios have a much tighter structure and would need longer incubation times. However, we could not see any differences in the results from the two water-cement ratios used in our measurements.
- Samples of concrete contain larger rock aggregate that normally has a very low porosity and will not hold much VOC. This will give problems for the sample preparation, as headspace vials are rather small.
- When samples are crushed and sieved rather large fractions of the more volatile compounds may be lost by evaporation. In a preliminary study (Hjellström et al.2002) we found that it was not possible to get high recoveries when the VOCs were mixed into the cement mortars. This may, however, have been caused by other factors, e.g. leakage, as similar results was found in the present study when the samples were stored prior to the measurements.

We see several uses the type of method we have been working with:

1. To investigate concrete constructions that has been exposed to VOCs for long time periods. One example that has recently been investigated in Sweden (Sjöberg, 2001) is n-butanol and 2-ethyl-1-hexanol from the degradation of PVC flooring/adhesive laid on concrete. Such information is interesting as it gives an idea of the amounts of VOC that may be emitted from such a floor.

2. To investigate old industrial buildings in which the concrete floors may have been contaminated by oil wastes (auto repair shops), PCB (transformer manufacturers), etc. When such buildings, as is quite common today, are rebuilt to become offices or apartments it is important to assess that hazardous substances stored in the floors cannot contaminate the indoor atmosphere. Measurements with a FLEC (Gustafsson 1999) on a floor can be used to find the emission rates at a certain time, and the present method can be used to measure the total concentration on different levels of a floor to calculate the total amounts stored in a floor.
3. As a laboratory method for testing for VOC emissions from cement-based materials. It is well known that ordinary Portland cement concrete is a material with low emissions, but the present trend with an increased use of organic additives, waste and recycled materials in concrete there is a need for new rapid methods to test for emissions. A problem with such a use is that the material has to be heated for the MHE method and that volatile substances may be formed during the heating. One could thus find VOCs that would not be formed in the material at normal use.

CONCLUSIONS

We have developed a multiple headspace gas chromatography method for the quantification of VOCs in concrete. The method seems to work well for n-propanol, n-butanol, n-hexanol, 2-ethyl-1-hexanol, pentadecane and octadecane, but the recoveries are rather low (about 50%) indicating that there is some factor that we not control properly. Further development and documentation of the method technique is also necessary to deal with the problem of over-pressure for moist samples.

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Paper III

Emission of Ammonia from Cement Ground with Different Grinding Aids

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Emission of ammonia from cement ground with different grinding aids

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Abstract

This study concerns the occasionally occurring ammonia odour from fresh cement and concrete. We have measured early emissions of ammonia from cements ground with different grinding aids, some containing amines. Measurements have also been made on mortars made with the different cements. Ammonia emissions have been measured by absorption in diluted sulphuric acid and detection by spectrophotometry and ion chromatography. Nitrogen analyses of cements and raw materials were also made. One of the ground cements showed higher early ammonia emissions both from dry cement and from mortar. There were also some ammonia emissions from cements ground without nitrogen containing grinding aids. Nitrogen analysis of the raw materials showed that their contributions to the nitrogen contents of the cements were, with the exception of one cement, larger than that from the grinding aids. The result indicates that one may get high ammonia concentrations in closed silos etc., but that the ammonia emissions from concrete in buildings is negligible.

Introduction

An important step in the production of cement is the grinding of the clinker in ball mills together with gypsum and possibly some additive materials like limestone or fly-ash to a fine powder. The size distribution of the grains depends on the wanted properties of the cement. The average particle diameter in ordinary Portland cement is in the order of 15 μm. Milling is an energy intensive operation – milling normally consumes 120 MJ electric energy per ton cement - and decreasing the energy input to the mills is one important way of decreasing the environmental impact of cement manufacture.

Optimising mill operation consist of a number of activities including among other things the optimisation of the use of grinding aids, chemical compounds that work as surfactants. They separate the particles from each other both in the mill, raising the throughput, and after the grinding, improving the flowability during transport of the cement. The use of grinding aids can decrease the energy consumption of a mill up to 25% depending on the type of mill and the type of cement. There is thus a large environmental incentive to use grinding aids. In addition to that, some cement grinding aids are formulated to interact with the hydration kinetics of the cement, for the purpose of controlling the set and strength development.

Commercial grinding aids are often aqueous solutions of more than one surface-active compound, of which the most common are:

- Triethanol-amine and other amine alcohols.
- More amine concentrated compounds like tetra- and penta-amines.
- Ethylene glycol and propylene glycol.

Grinding aids are added in amounts in the order of 0.02% - 0.05% of the cement mass.

As seen above, most grinding aids are nitrogen-containing amines with rather high boiling points. However, there is a possibility that they can be degraded in the mills or in the concrete to more volatile substances. During grinding the temperature is raised above 100°C and, although the cement is cooled to 50-60°C after the grinding, it is still warm when it is stored in the silo. The amine compounds in the grinding aids may degrade to either ammonia or more volatile amines, which often are very odorous compounds. Although the added concentrations are low it may be that these compounds are responsible for the, sometimes, reported smell of ammonia in cement packing plants and during concrete manufacturing. There is also a possibility that the grinding aid compounds will degrade in the very alkaline environment of the pore solution of the cement paste, giving emissions of odorous compounds in buildings made of concrete.

Generally compounds that are stable will be left in the product for a long time, whereas unstable compounds may degrade to more volatile substances that leave the product as emissions. The compounds in the studied grinding aids above have different stabilities. The ethanolamine solutions have high pH and the compounds decompose at temperatures above 50°C (Hiroyuki et al. 1997) and also after long storage at room temperature. The more concentrated amine compounds also have high pH. These compounds have higher boiling points, i.e. they are less volatile. Still, the higher amines can be oxidized, thereby able to release ammonia or volatile amines. The stability of the amine products probably depends on the reaction path used in the production of the compounds and there can be ammonia or ammonium salts left in the product depending on refining. Diethylene glykol is a colourless and almost odourless liquid that easily absorbs moisture. It is stable, not very volatile and it does not contain nitrogen so it cannot be a source of ammonia emissions. It is probable that some commercial grinding aids have a quite large content, e.g. 10%, of impurities that are not declared in the data-sheets. It is also probable that some of these impurities are less stable than the main components.

There is an increased interest in issues concerning indoor air quality and related questions, e.g. indoor air chemistry, and emissions from degraded building materials. Although concrete is generally assumed to be a good material for healthy buildings, its high moisture and alkali levels can cause problems if the initial drying is not properly made.

There has been some concern over the emissions of ammonia from concrete to indoor environments, especially in China and Japan. (Mitani et al. 1966) and (Kurosaka 2002) report that museum objects can be damaged by ammonia emitted from concrete. However, it is uncertain what the origin of the ammonia is. Mitani et al. (1966) have tested an ammonia absorbing paper to cover all internal concrete surfaces with. Kurosaka (2002) gives a rather strange guidance to how a museum should be planned to reduce the risk of damaging museum objects by ammonia. Bai et al. (2003) report ammonia concentrations of 0.4-5.9 mg/m^3 in Chinese buildings made with concrete containing carbamide as an anti-freeze agent.

In Europe and the US ammonia emissions from concrete made with fly ash, have been investigated. Fly ashes from coal power plants can contain ammonia as ammonia is utilized to reduce emissions of nitrogen oxides. Koch and Prenzel (1989) tested screeds with fly ash and found only very low and rapidly decreasing emissions. Spanka and Thielen (1999b) investigated emissions of ammonia, volatile organic compounds and formaldehyde from cement with fly ash and two different grinding aids. They report that within 14 days from fly-ash in a concentrated sodium hydroxide solution, about 60% of the measured nitrogen content comes out as ammonia. From cement pastes with 20% fly-ash and with three different water to cement ratios, about 30% of the total ammonia content was emitted during 7 days.

The aim of this study is to compare the emission of ammonia from cements ground with different grinding aids. Measurements have been made on the freshly ground cements (after one day), cement during storage (after three to eight days), and on mortar made with the cements.

Materials

Portland cement clinker was taken from the normal production at Cementa AB, Slite, Sweden. A microscopy study of the clinker phases was made to prove that there were normal circumstances during the production of the clinker. The grinding aids (Table 1) were either acquired as fine chemicals or bought as commercial grinding aids.

Grinding

Cements were ground on a laboratory scale. Into a ball mill with a capacity of 50 kg were added 41.3 kg of clinker, 5 kg of crushed limestone, 2.37 kg of gypsum, 1 kg of slag, 0.3 kg of iron sulphate and 17.5 g of grinding aid (diluted 1:2). This was ground for 90 minutes. No ammonia odour was recognized during the grinding procedure. Afterwards the cement was cured in a laboratory oven at 120°C for one hour to simulate the high temperatures in industrial mill that commercial cements are exposed to. Between the grindings, the mill was cleaned by running it open until no more cement came out of the mill. We did, however, suspect that grinding aids from the previous milling could be left in the mill, so for the latter two runs two and three on cements E and F (Table 2) the mill was cleaned by milling for 90 minutes with sand the second time and clinker the third time.

Casting of cement mortar

Into the bowl of a Hobart mixer were added 875 g cement, 2100 g coarse sand, 525 g fine sand and 306 g or 525 g of water, to get mortars with water to cement ratios (w/c) of 0.35 and 0.60 respectively. After dry mixing for 30 seconds and wet mixing for two minutes, the mortar samples were cast in Petri dishes of glass (150 mm diameter and 15 mm deep, mortar mass 780 g) and in metal buckets (mortar mass about 1 kg).

Table 1. An overview of the different grinding aids used in the study. The estimated nitrogen contents have been calculated from data in product data sheets.

Cement	Grinding aid	Appearance	% nitrogen (estimated)
A	Commercial product, triethanolamine	Colourless, odourless	8,0
B	Commercial product containing mainly triethanolamine; but also some higher amines	Yellow, weak odour	8,2
C	Commercial product; mainly monoethanolamine	Brown, weak odour	14
D	Commercial product; triethylenetetraamine and other higher amines	Yellow-brown, strong ammonia odour	39
E	Diethylene glycol (p.A., >99.0%, Merck)	Colourless, odourless	0
F	No grinding aid	-	-

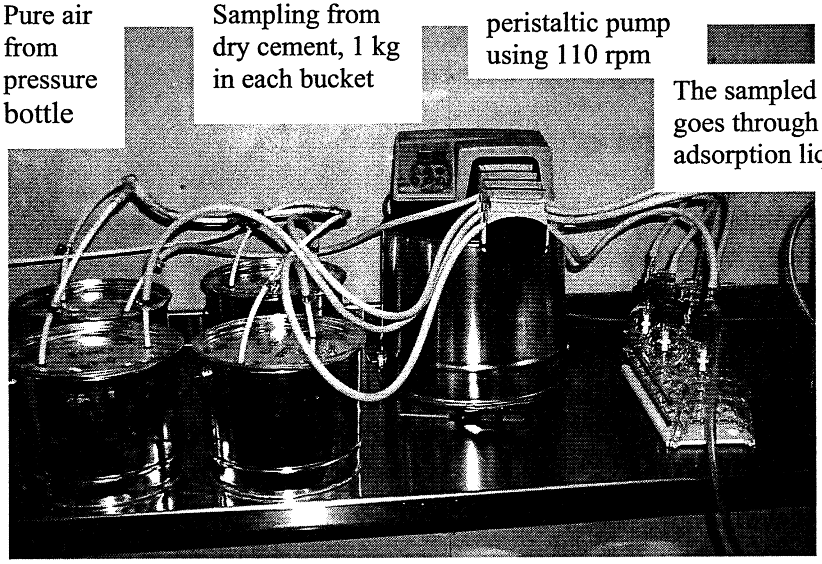
Methods

Sampling of ammonia from cement powder

Lots of one or two kg of the cements were charged into metal buckets that were sealed with tight metal lids. Sampling of ammonia from all such samples was performed at one and eight days after the cements were produced. Some samples were also sampled at three days. During sampling air was drawn out of the buckets and the flow rate was controlled by peristaltic pumps. The sampled air was pumped into impingers with 0,01 M sulphuric acid solutions.

The air drawn out of the samples buckets was continuously replaced by synthetic air that was supplied through an overflow device that ensured that the upstream pressure was close to the ambient pressure so that the flow rate was only controlled by the downstream pumps. The set-up is shown in Fig. 1.

Sampling was made with flow rates of 350-400 ml/min during four to five hours. The actual flow rate was measured for each measurement where the air left the impingers with the soap bubble technique. In that technique the gas stream is led through a burette and the time for a soap bubble to move a certain length corresponding to a certain volume is measured. The flow was measured both at start and in the end of the long samplings and at least three times on each occasion. For some samples the ammonia measurements were divided into one short and one longer measurement. For those samples are both results presented in table 2 in the result section. Otherwise is only one sampling made and the result is the total emission from the cement at that time.



Pure air from pressure bottle

Sampling from dry cement, 1 kg in each bucket

Four channel peristaltic pump using 110 rpm

The sampled gas goes through the adsorption liquid

Figure 1. The sampling of ammonia from dry cements in sealed buckets.

We have tested the equipment by measuring recovery of ammonia from a flow of nitrogen with a known (1000 ppm) ammonia concentration. About 70 % of the ammonia was detected in the FIA analysis. There was no breakthrough of ammonia through the first impinger (less than 0.4 %), when two impingers in series were used.

Sampling of ammonia from mortar

Ammonia emissions from the mortar samples were sampled using FLEC emission cells (Gustafsson, 1999) and plaids, bottom parts, in which the Petri dishes fitted (150 mm diameter, 15 mm deep). The cell was connected to synthetic air and an absorbent solution in the same way as the sampling from the cement powder described above. The ammonia emission rate was measured from the mortars after 1 and 14 days using flows of about 380 ml/min for about 5 h. Before the measurements the mortars were stored open in 23°C and 50% relative humidity. The ammonia concentration in the air above the mortar sample was also measured after four weeks. Before these measurements the samples were closed for 4–6 weeks.

Quantification of ammonia

The concentration of ammonium in the absorption solutions was analysed by two techniques:

- A total of 200 analyses with Flow Injection Analyses (FIA) were made at Cementa Research AB with a FOSS Techator, 5012 Analyzer. In this technique reagents form a coloured species with ammonium that are detected by spectrophotometry. The accuracy is 15%.

- A total of 105 analyses with Ion Chromatography (IC) were made at Analyscentrum, Stockholm with a Dionex IC. In this technique the ions are separated in a column. The column used was a Dionex IonPac CG15 (4x15 mm) + Dionex IonPac CS15 (4x250 mm). The detector used was Dionex ED40 Electrochemical Detector. The accuracy is 15%.

In the result section only the FIA results are shown as the IC results gave very much the same results. Differences between results with FIA and IC were about 10% and this is less than the standard deviation between double/triple samples given for FIA results in Table 3.

Method for quantification of grinding aids in cement

This method analyses the amine content. In this study it was used to determine the nitrogen contents of both the raw materials and the cements ground with different grinding aids. The organic amine compounds are oxidized by potassium permanganate in a high pH environment where ammonia is formed. By distillation the ammonia is transferred to ammonium in an acidic solution. Using Nesslers reagent (an alkaline solution of mercury iodide in potassium iodide) the amine content is estimated by spectrophotometry. The accuracy is 6% within a concentration range of 50 to 500 ppm of the grinding aid used as a reference, which correspond to an ammonium concentration of 8 to 80 µg in 50 ml.

Kjeldahl method for quantification of nitrogen

The Kjeldahl method is commonly used to determine the nitrogen content of foods, sewage sludge and other organic materials. In this study it was used to measure the nitrogen contents of the raw materials. It gives the content of organically bound nitrogen and dissolved ammonium. By oxidation with sulphuric acid and boiling, the nitrogen containing compounds in samples are dissolved. Then the pH is raised by addition of sodium hydroxide and ammonia is formed. By distillation the ammonia is transferred to ammonium in an acidic solution. The nitrogen content is then estimated by titration. We believe that organic nitrogen containing compounds in our cements and raw material samples should dissolve in the 4 M sulphuric acid, but mineral-bound ammonium possibly needs fluoric acid to dissolve. The accuracy in the method is 3% in ammonium-bound nitrogen concentrations between 3 – 150 mg/l.

Results

The results of the emission measurements with the spectrophotometric FIA method are shown in Table 2 (as noted above the ion-chromatographic method gave very much the same results). For cements the emissions measured with FIA after 1 and 8 (in some cases also 3) days are summed. The relation between emissions from one to three days is 1:1 and from one to eight days it varies from 1:1 to 1:5. Values for long and short sampling of the cements and also the sum of them are given. The relation between emission measured by long and short sampling varies between grinding aids. For E the emission measured by short sampling is dominating, especially after eight days. For the other cements the relation is the opposite.

Results from ammonia measurements on cements and mortars of w/c 0.35. The ammonia emissions from cement correspond to 1 kg cement and for the equilibrated mortar the emissions relate to 1 kg sample. Emission rates from mortars were measured with the FLEC method after 1 and 14 days. Air concentrations of ammonia over mortars were measured with FIA after 4 weeks. Note that it is not possible to directly compare the results in different columns of Table 2 as the emissions have been quantified in three different ways. See Method section for complete descriptions of measurement methods.

Table 2.

Product A-F Date of grinding Replicate a-b or a-c			From cement			From mortar		
			Short sampling	Long sampling	Sum of long and short sampling	Emission rate, 1 day	Emission rate, 14 days	Equilibrated, 4 weeks
			µg	µg	µg	µg/(m^2*h)	µg/(m^2*h)	µg
A	20 Jan		2,6	6,6	9	47	20	2,0
		b	1,2	5,9	7	71	0	1,0
B	30 Jan	a	5,9	10,8	17	37	7	5,7
		b	5,1	4,1	9	78	0	1,1
		c	0,4	3,5	4	108	0	1,5
C	21 Jan	a	5,1	11,8	17	84	0	1,6
		b	5,3	10,6	16	93	0	1,6
D*)	13 Jan	a	8,4	190	198	641	93	2,0
		b	16,2	236	252	352	8	2,5
E*)	27 Jan	a	21,2	2,7	24	249 275**)	0	1,6
		b	14,5	2,6	17	271 191**)	0	0,9
	18 Mar	a^{II}		32	32			
		b^{II}		47	47			
	22 Apr	a^{III}		33	33	50***)	0***)	
		b^{III}		17	17	260***)	0***)	
F	14 Jan	a	1,2	7,4	9	71 24**)	17	1,8
		b	1,6	11,0	13	80 164**)	0	1,0
		c	1,0	10,0	11			
	18 Mar	a^{II}		36	36			
		b^{II}		38	38			
	22 Apr	a^{III}		27	27	590***)	4***)	
		b^{III}		22	22	690***)	42***)	

*) Measurements on cement were made after 1, 3 and 8 days.

**) Performed on mortars of the cement that had been stored for nine months.

***) Measurements are made on mortars of the cements ground in April and stored for six months.

Results of the nitrogen analyses of the raw materials are given in Table 3 and results from the measurements with the method for quantification of grinding aids in cement is presented in table 4.

Table 3.

Chemical analysis of the nitrogen content of the raw materials by the Kjeldahl method is shown. The contribution of nitrogen from the raw materials is calculated.

	Nitrogen content (mg/kg raw material)	Nitrogen contribution in the cement (mg/kg cement)
Clinker	40	33
Crushed limestone	110	11
Slag	190	3.8
Gypsum (natural)	<40	≤ 1.9
Iron sulphate	<40	≤ 0.24
Sum		50

Table 4.

Estimated and measured nitrogen content in the cements ground with different grinding aids. The content of grinding aids was measured with the method described under the section "Method for quantification of grinding aids in cement".

Cement	Amount of grinding aid added at grinding (mg/kg)	Estimated nitrogen content in the cements (mg/kg)	Measured content of nitrogen in cement (mg/kg)
A	177	14	12
B	176	14	7,8
C	176	25	5,3
D	175	68	31
E	177	0	0,5
F	0	0	2,4

Generally, samples of w/c 0.60 showed 50-70% lower emissions than those with w/c 0.35. On cement D, the emission from w/c 0.60 where only half of the emission from w/c 0.35. On cement A, the emission from w/c 0.60 was two thirds of that from w/c 0.35.

Discussion

It is seen in Table 2 that cement ground with grinding aid product (D) has higher ammonia emissions than the other cements. This is also the product that has a strong odour of ammonia, i.e. it contains free ammonia and/or easy degradable amines. The other grinding aids do not give higher ammonia emissions than the cement ground without a grinding aid. Grinding aid products A-C thus seem to be stable in the cements.

For the mortar the situation is similar, as cement D gives higher emissions than the other cements. The emission rate is also unexpectedly high from the mortars made with cement E and F, where E were ground with diethylene glycol that does not contain nitrogen and in cement F no grinding aid was used. Repeated measurements show the same result. One explanation could be that the physical properties of mortar were dependent on which grinding aid that was used. It is, for example, known that the ethanol amine grinding aids acts as plasticizers and disperse the cement grains also in the fresh cement paste. This could possibly influence porosity, which in turn could influence the desiccation of the mortars. Diethylene glycol is sometimes used in concrete to reduce shrinkage by preventing evaporation. This could possibly prevent surface desiccation and promote ammonia emission. Unfortunately we have no information on the desiccation rate of the mortar samples.

The different measurements made in this study have been made in different ways, e.g. equilibrium concentrations and emission rates, so it is not possible to calculate the total amounts of ammonia released from the samples.

However, we have made approximate calculations by making the following assumptions:

1. The total release of ammonia from 1 kg of the cements during the first eight days equals the values given in Table 2.

2. The time dependency of the release from the open mortar samples during the first 14 days after casting is approximated with an exponential decay with a time constant of 9 days. This time constant is the mean of the time constants 9, 6 and 12 days of mortars A, D and F for which the 14 days emission rates were not zero (if it is zero no time constant can be calculated). The total emission was then calculated as the integral of the emission rates from casting to infinite time times the surface area of the mortar samples. The values were than scaled to units of emitted ammonia per kg cement.

3. The air concentrations over the mortars after four weeks were not used in the calculations as they were low and were assumed to be included in the previous integral.

Table 5 shows the results of these rather approximate calculations. It is seen that for all cements, including cement D with the highest emissions, the total emissions of nitrogen are only a small fraction of the nitrogen added to the cements with the grinding aids or present in the raw materials.

Table 5.

The ammonia emission in relation to the amount of nitrogen added by the grinding aid. The amounts are related to 50 kg of cement. To avoid underestimation from the cement twice the amount that was measured during the first eight days has been used in the calculation.

	Added via grinding aid	Emission from cement	Emission from mortar	Emission in relation to nitrogen added via grinding aid	Emission in relation to total nitrogen content (from both grinding aid and raw material)
	g NH_3	mg NH_3	mg NH_3	%	%
A	0.86	0.8	61	7.2	1.8
B	0.85	1.0	39	4.7	1.2
C	1.47	1.6	35	2.4	0.9
D	3.39	22	360	11	6.5
E	0	2.8	96		4.0
F	0	2.2	113		4.6

It has been reported that workers at cement plants have complained about ammonia odour, e.g. in silos and other poorly ventilated spaces. The present results clearly indicate that quite high amounts of ammonia can be emitted from large amounts of cement. For example, if 100 ton/h of warm cement is passed on a conveyor belt through a cubical room, 10 m on each side, the ventilation rate is 10 air change per hour, and 200 μg ammonia is released from each kg of cement (the emission measured on cold cement D during the first 8 days), the resulting ammonia concentration will be 2 mg/m^3. This is in the same order of magnitude as both the odour detection threshold for ammonia, which is 4.07mg/m^3 (Jensen and Wolkoff 1996) and the mucous membrane irritation threshold of 6.44 mg/m^3 (Jensen and Wolkoff 1996).

The mucous membrane irritation threshold is calculated as 3% of the concentration that gives a 50% reduction in respiratory rate in mice (Schaper 1993). Much higher concentrations can be reached in closed or poorly ventilated spaces like silos and ships. The present results indicate that the ammonia concentrations in air in cement plants will be significantly reduced if a grinding aid with free ammonia or unstable amines is replaced with a more stable product.

The measured emission rates from mortar can be used to estimate a worst case ammonia concentration in a building with open mortar/concrete surfaces. We take a normal room with a floor area of 4 m x 4 m, a height of 2.5 m (40 m^3), with an air change rate of 0.5 1/h, and with one wall made of exposed mortar rendering (10 m^2). The emission at day 1 from mortar D was 500 $\mu g/(m^2h)$. With the above figures this will give a steady-state ammonia concentration in the room of 250 $\mu g/m^3$, i.e. lower than the odour detection threshold and the mucous membrane irritation threshold. As indicated by our measurements at 14 days and 4 weeks after casting, the ammonia emissions from a rendering or a concrete at the time people move into a building will be negligible.

The present study shows that cements and mortars emit ammonia and that quite high concentrations can be reached in places where fresh cement is handled. On the other hand ammonia emission in buildings does not seem to be a problem. As only a small fraction of the nitrogen in the raw materials and the grinding were emitted, it is clear that the major part will end up in the mortar/concrete.

Future research in this field could aim at answering some of the following questions:

- Is the nitrogen in the raw materials stronger bound than nitrogen from the grinding aids?
- For how long will the nitrogen stay in the cement based products?
- Can the reported ammonia emissions from water damaged concrete slabs come from grinding aids?

- Are the nitrogen quantification methods used robust? Will they measure nitrogen from both raw materials and grinding aids in the same way?
- What is the mechanism that gives higher ammonia emissions from mortar (but not from cement) when the cements are ground without nitrogen containing grinding aids?

Conclusions

The ammonia emission differs from cements and mortars when different grinding aids are used and is not only dependent on their nitrogen content. Although the ammonia released from fresh cement in a cement plant can give problems if the ventilation is poor, our results indicate that ammonia emitted from concrete or mortar does normally not give any indoor air quality problem.

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