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Heavy Metals in Cement and Concrete Resulting from the Co-incineration of Wastes in Cement Kilns with Regard to the Legitimacy of Waste Utilisation

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Abstract

Heavy metals in cement and concrete resulting from the co-incineration of wastes in cement kilns with regard to the legitimacy of waste utilisation

Aim of this project was to investigate the impact of the use of secondary fuels, secondary raw materials and blending agents on trace element concentrations in cement and concrete. Furthermore, the aim was to investigate under which conditions and to which extent the incorporated trace elements can be released into the environment. Additionally, it should be proofed, whether regulations, standards, directives, etc. for the production of cement and corresponding construction products contain specific requirements for pollutant loads.

The study has shown, that presently used secondary raw materials and fuels result in some cases in a slight increase in trace element concentrations in cement. However, a general assessment of the use of wastes in cement production and of its impact on trace element input can not be performed. Furthermore, future developments can hardly be estimated.

The release of trace elements from concrete elements is negligible small during the phase of use. An increased release of trace elements is possible under special assumptions after demolition. However, the present knowledge is not sufficient for a definite assessment.

Existing regulations concerning the production and use of cement do not presently contain defaults for allowed concentrations of pollutants. However, changes can be expected in future due to demands which are presently worked out for the EU.

Zusammenfassung

Untersuchung des Einflusses der Mitverbrennung von Abfällen in Zementwerken auf die Schwermetallbelastung des Produktes im Hinblick auf die Zulässigkeit der Abfallverwertung

Ziel des Vorhabens war es, den Beitrag von Sekundärbrennstoffen, Sekundärrohstoffen und Zumahlstoffen zum Spurenelementgehalt von Zement und Beton darzustellen. Des Weiteren sollte untersucht werden, unter welchen Bedingungen und in welchem Maße die eingetragenen Spurenelemente in die Umwelt freigesetzt werden können. Zusätzlich sollte geprüft werden, welche Vorschriften, Normen und Richtlinien, usw. für die Produktion von Zement und den damit hergestellten Bauprodukten spezielle Anforderungen zu Schadstoffgehalten enthalten.

Die Untersuchungen ergaben, dass die derzeit eingesetzten sekundären Einsatzstoffe einen geringen Anstieg der Konzentration einzelner Spurenelemente im Zement zur Folge haben. Eine Bewertung des Abfalleinsatzes bei der Zementherstellung und seiner Auswirkungen auf den Spurenelementeintrag kann jedoch nicht pauschal vorgenommen werden. Weiterhin lassen sich zukünftige Entwicklungen schwer abschätzen.

Die Freisetzung von Spurenelementen aus Betonbauteilen ist während der Nutzungsphase vernachlässigbar gering. Nach dem Abbruch ist ein erhöhter Spurenelementaustrag unter speziellen Annahmen denkbar. Der heutige Wissen-stand reicht aber für eine abschließende Bewertung nicht aus.

Die existierenden Vorschriften für die Herstellung und Verwendung von Zement enthalten zurzeit keine Vorgaben für zulässige Schadstoffkonzentrationen. Allerdings sind zukünftig Änderungen zu erwarten, da diesbezüglich auf europäischer Ebene derzeit Anforderungen erarbeitet werden.

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1 Introduction

1.1 Problem definition

Cement is an important binding agent for construction industry and is produced world-wide in large amounts. In 2000, about 35.2 million t of cement were manufactured in Germany and about 323 million t in Europe [BDZ, 2002].

A central process step during the manufacturing of cement is the production of the intermediate product clinker. For this production, inorganic raw materials are burnt at temperatures in the range of 1,500°C. In order to reduce the costs of this energy-intensive process which has a high share in the manufacturing costs of cement, regular fuels like coal, oil, and gas are increasingly substituted by different types of waste.

Co-incineration of waste to substitute regular fuels started more than 20 years ago with the use of waste oil and used tyres. In the last 10 years, use of waste in the German cement industry has increased. In 2001, secondary fuels covered about 30 % of the total energy consumption. As reported by the German Cement Works Association [VDZ, 2002], 237,000 t of used tyres, 245,000 t of meat and bone meal and animal fat, and 128,000 t of waste oil were used in cement plants together with approximately 420,000 t of fractions of industrial and municipal waste. The share of secondary fuels in the total use of fuels in cement plants is expected to increase further.

In cement manufacture, use of waste is not restricted to the use as an energy carrier in the burning process of clinker production, but waste is also used as an alternative inorganic raw material. A high proportion of primary input materials can be substituted by varying proportions of secondary raw materials and fuels. For this reason, a wide range of secondary raw materials and secondary fuels can be considered for use by cement industry.

An additional influence on the amounts of waste used in cement plants is expected to result from two current European legal cases (C-228/00 and C-458/00) [Kaminski and Figgen, 2003]. The corresponding judgements were rendered by the European Court of Justice on February 13, 2003. In accordance with these judgements, it can be assumed that the use of waste in cement plants will increase. On the other hand, the possibilities of using waste in solid waste incinerators are expected to be restricted.

However, unrestricted use of waste in cement manufacture is not possible. The required properties of manufactured cement are ensured by exactly specified fractions of main constituents in the cement. In particular, the incineration residues of the used secondary fuels, which are transferred predominantly into the cement, must be accounted for accordingly.

Waste used as secondary fuel or as a substitute of inorganic raw material may contain varying trace element concentrations compared to conventional raw materials and regular fuels. The use of wastes inevitably leads to the question of where the trace elements of the wastes remain. The presently used procedures for cement manufacture cause the trace elements to be either transferred into the product cement or emitted with the exhaust gas into the environment.

Co-incineration of waste in cement industry is subject to some controversy among experts, in politics, and parts of the society. Due to insufficient and lacking knowledge of the associated effects on the environment, the discussion is not always objective. Since the flue gas cleaning systems of cement plants are designed for a manufacturing process and not for waste incineration, the concern arises that the use of waste may possibly lead to increased emissions of trace elements.

Additional points of discussion result from different legal regulations. In the past, the permissible air emissions of cement production without using waste were based on the "TA Luft" (clean air) regulations of 1986, which were updated first by a dynamic clause and then replaced by a revised version in 2002. For the co-incineration of waste, the far stricter limit values of waste incineration are considered by the mixture calculation as specified by the 17th Federal Immission Control Ordinance [17. BImSchV]. Its practical application, however, led to a number of problems. In this respect, extensive changes will result from a new European Union directive to be adopted.

When using waste in cement manufacture, it must be guaranteed that this use is proper and not harmful in the sense of the German Waste Management and Recycling Act (Kreislaufwirtschafts- und Abfallgesetz). Apart from the discussion of effects of the use of waste on air emission, plant operation, and product quality of the cement clinker, the question to which extent trace elements are transferred into the cement and potential environmental impacts becomes increasingly important. This does not only concern the use of secondary fuels, but also the use of secondary raw materials as an alternative to raw meal, an interground additive for cement manufacture or as an aggregate for concrete production.

Mobilisation of trace elements in concrete or other construction products represents a major aspect in the assessment of the potential environmental impact due to the influence of rainwater, groundwater or other effects that accelerate weathering. The factors influencing this leaching behaviour are very complex. International and national leaching measurements performed by cement industry and institutes of construction materials research indicate a reliable fixation of trace elements in the short and medium term. However, it is not yet clear to which extent all relevant factors have been taken into consideration already. It is also uncertain whether these factors are significant to the service life and post-service phases of buildings. Particular uncertainties exist in the assessment of the long-term behaviour of trace elements in construction materials.

1.2 Fundamentals of the Production and Use of Cement

Production of Cement

In the following sections, the production process of cement will be described briefly. Production of cement may be subdivided into the areas of supply of raw material, burning of cement clinker in the rotary kiln, and actual cement production by adding interground additives. Figure 1 shows a simplified representation.

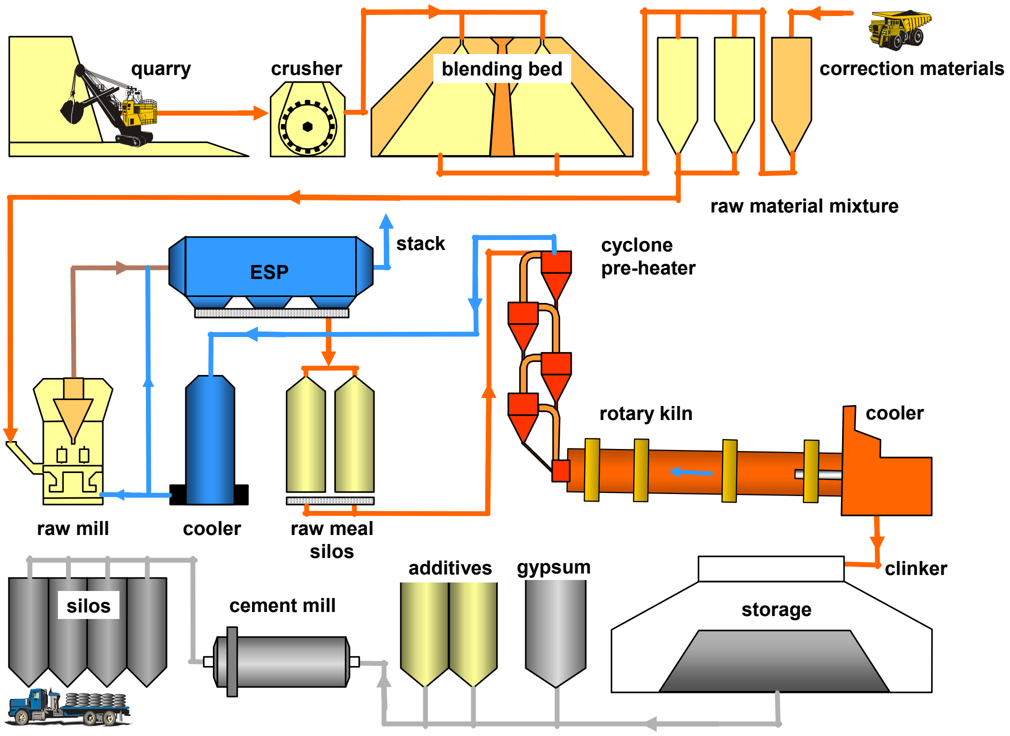


Figure 1: **Schematic representation of cement production.**

Cement production starts with the extraction of the raw materials limestone, marl, and clay and their subsequent pre-crushing in the quarry that is usually located in the vicinity of the cement works. With the ratio of raw materials being specified exactly, a mixture is produced, if necessary, by adding correction materials, such as sand, iron ore, and clay. Apart from natural raw materials, waste materials containing lime, aluminate, silicate, and iron increasingly gain importance as raw materials substitutes.

This mixture of raw materials is milled to raw meal in a raw mill and, at the same time, dried with the residual heat of the kiln offgases. In the downstream electrostatic precipitator (ESP), the raw meal is separated and subsequently transported to raw meal silos. Via a pre-heater, in Figure 1 a four-stage cyclone pre-heater, the dust-like raw meal is fed into the rotary kiln. By means of the burning process at 1,250 to 1,500°C, clinker granules are formed. The energy required is supplied by the combustion of coal, oil, gas, or secondary fuels in a burner at the end of the rotary kiln (primary combustion) and partly also at the beginning of the rotary kiln (secondary combustion). The hot flue gases generated by combustion flow through the rotary kiln and pre-heater in opposite direction to the solids. Selected technical data of kiln systems are given in the Annex in Table A12 and Figure A1. The clinker leaving the rotary kiln has to be cooled down. For this purpose, grate or planetary coolers are installed.

Clinker represents the most important constituent of the various types of cement produced by the addition of gypsum and other interground additives (limestone, granulated blast-furnace slag, coal fly ash, trass, etc.) and subsequent crushing.

The setup of large-scale plants varies and is more complex than shown in Figure 1. Some large-scale plants are equipped with calciners. In these vertical carbon entrainment reactors that are arranged between the cyclone pre-heater and the rotary kiln the chemical reactions required for clinker production take place. In these cases, length of the rotary kiln is reduced.

Apart from the so-called dry process shown in Figure 1, semi-dry Lepol kiln systems are operated in Germany. Here, the raw meal is supplied in the form of pellets, and a grate system serves as pre-heater.

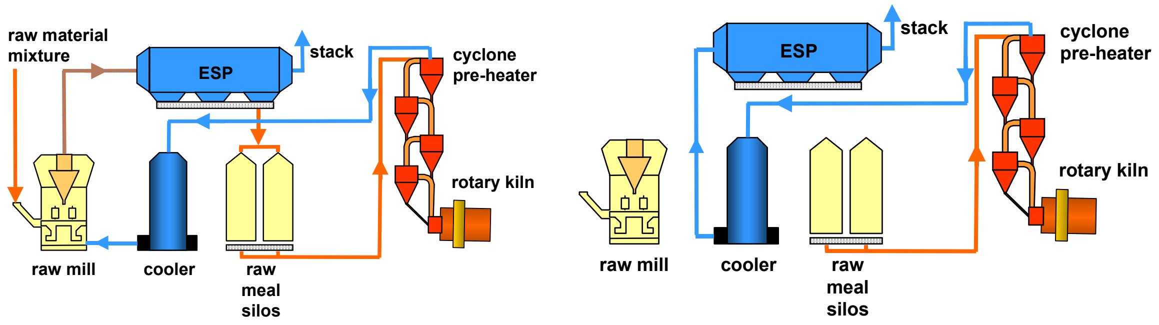
Special Features of Cement Production Plants

In contrast to other (combustion) plants, e.g. power plants or waste incineration plants, cement production plants and in particular those with cyclone pre-heaters are characterized by an enhanced formation of materials cycles. This formation is based on the varying volatility of the trace elements contained in the raw materials, fuels, and wastes. In this respect, it is distinguished between the inner and the outer circuit.

The ***inner circuit*** is established between the pre-heater and the rotary kiln. At the temperatures prevailing in the rotary kiln, the volatile compounds enter the gas phase and are transported into cooler sections of the pre-heater together with the gas flow. There, they condense on the raw meal and are transported into warmer sections again. Accumulations occur, which may reach a multiple of the initial concentration.

The ***outer circuit*** additionally comprises the mass flow, including the raw mill and deduster downstream of the pre-heater. The outer circuit is deemed to be closed when this mass flow is added to the combustion material again.

In this context, the operation modes of “compound operation” and “direct operation” shown in Figure 2 are of major importance. During normal operation, these modes are run alternately, depending on the need. During ***compound operation***, shown in Figure 2 on the left, the dust-containing offgas from the cyclone pre-heater is used for drying and transporting the raw meal from the raw mill. No addition of cooling takes place in the offgas cooler. The raw meal and fly dust from the kiln system are separated jointly by the electrostatic precipitator and passed on to the raw meal silo.



compound operation

direct operation

Figure 2: Compound and direct operation in cement production.

During ***direct operation*** (Figure 2 on the right), the raw mill is not used. The raw meal is fed into the kiln from the silo. The dust-containing offgas from the kiln is cooled down in the offgas cooler by the injection of water and subjected to subsequent dedusting in the electrostatic precipitator. The separated dust and, hence, the trace elements contained in it are partly returned to the cement production process during cement milling and partly added to the raw meal again (not shown in Figure 2).

These different modes of operation considerably influence the temperatures and material flows between the mill, kiln system, and electrostatic precipitator of the plant. These changes also affect the trace element mass flows in the plant. Increased offgas temperatures during direct operation cause higher mercury emission levels than in the compound mode. Moreover, regular alternation of the operation modes results in weekly cycles of mercury flows in the cement plant [Schäfer and Hönig, 2001].

Another possibility of controlling material flows in cement production plants are so-called bypasses. Using these bypasses, partial flows can be removed specifically so as to reduce the concentrations of certain substances. Three bypass variants are represented schematically in Figure 3.

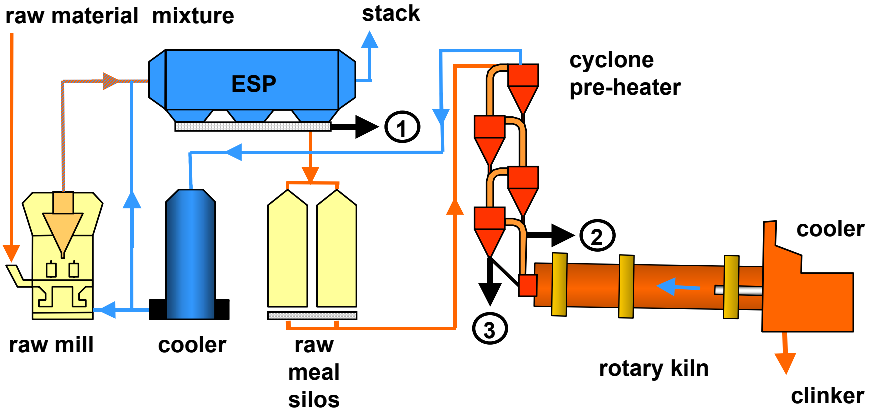


Figure 3: **Schematic representation of bypass variants (1: dust bypass, 2: hot gas bypass, 3: hot meal bypass).**

The ***dust bypass*** (1) serves to interrupt the outer circuit. Part of the filter dust is removed and, hence, does not enter the raw meal. Thus, the trace element cycle is relieved. The discharged material, however, usually enters the cement as an interground additive.

Relatively high concentrations of alkali, sulphur, and halogen compounds may require a ***hot gas bypass*** (2) which in particular serves to remove alkali chlorides and sulphates. When using this bypass variant, part of the kiln offgases is removed between the rotary kiln and the lowermost cyclone of the pre-heater, cooled down to a variable extent depending on plant operation, and dedusted in some cases. After this, the offgases may be returned to the main gas flow, used for drying during milling or are discharged via the stack.

Another possibility of interrupting circuits in the kiln/pre-heater system is the ***hot meal bypass*** (3). In this case, part of the hot raw meal is discharged at the outlet of the lowermost cyclone. Compared to the hot gas bypass, a smaller technical expenditure is required at reduced heat losses. However, the hot gas bypass reaches a higher efficiency [Reiter and Stroh, 1995].

Hydration of Portland cement

Cement is a building material that independently hardens to cement paste under water uptake (= hydraulically). For the construction of buildings, cement is usually mixed with aggregates, mostly sand or gravel, and water. Following hardening, the aggregate grains are bound tightly by the hardened cement paste generated. Hence, cement is also referred to as hydraulic binding material. Depending on the formulation used, concretes or mortars with variable properties are generated.

Various types of cement are produced for construction industry. In Europe, 27 types of normal cement are standardized [DIN EN 197], which are composed of various mineral constituents. These differences in the composition influence the hardening behaviour of the individual normal cements. The most important type of normal cement in Germany is ordinary portland cement (OPZ, CEM I). In 2000, its share in total inland shipment reached about 62% [BDZ, 2002].

To describe the reaction of Portland cement with water (= hydration), the nomenclature usually applied in cement chemistry shall be used below. According to Table 1, the various oxides are abbreviated by letters.

Table 1: Nomenclature of cement chemistry.

Abbreviation	Chemical formula		Abbreviation	Chemical formula
C	CaO		$\overline{C}$	CO_2
A	Al_2O_3		$\overline{S}$	SO_3
S	SiO_2		H	H_2O
F	Fe_2O_3			

To put it in a simplified way, Portland cement consists of more than 90 mass% of milled cement clinker and a sulphate carrier, mostly gypsum ($CaSO_4 \cdot 2H_2O$) or $C\overline{S}H_2$. On the microscopic scale, however, cement clinker is no homogeneous material, but set up of various minerals, the so-called clinker phases. Apart from gypsum, four clinker phases are of decisive importance to the hydration of Portland cement: C_3S (“alite”), C_2S (“belite”), C_3A, and C_4AF. Each of these phases reacts when mixing cement with water. As a result, their structure is destroyed completely. Instead of the cement minerals originally suspended in water, new felted, water-containing minerals (hydrate phases) grow. They take up the place of the water-cement mixture and possess a high strength. The hydrate phases build up the hardened cement paste that binds the aggregate in concrete or mortar. Hardening of most constituents of other normal cements and some concrete additives is similar to that of Portland cement.

For a general understanding of the hydration of Portland cement, the sketch given above is sufficient. Detailed hydraulic reaction, however, is much more complicated, as each individual clinker phase reacts to different products. Moreover, the reactions influence each other.

Under water uptake, the calcium silicates C_3S and C_2S react to calcium silicate hydrate gel (CSH gel) and calcium hydroxide (CH, portlandite). The CSH gel is structured rather irregularly. It has a variable calcium, silicon, and water content and is responsible for the ultimate hardness of the hardened cement paste. The CaO/SiO_2 molar ratio of the CSH gel (C/S ratio) decreases with increasing age of the hardened cement paste. In young hardened cement paste, it amounts to about 1.8 to 2. In formulas, the C/S ratio is frequently given as index (e.g. $C_{1.8\text{-}2}SH$). The extremely large surface area of the CSH gel promotes the fixation of trace elements by sorption as well as physical and chemical incorporation.

Contrary to calcium silicate, the C_3A and C_4AF clinker phases containing Al_2O_3 or Fe_2O_3 react with both water and the sulphate carrier (e.g. gypsum, $C\overline{S}H_2$). These reactions control the setting behaviour of Portland cement and, hence, are important to e.g. the processing of concrete. Depending on the existing amount of calcium sulphate, either so-called AFt phases or AFm phases are generated by hydration. AFt is derived from “**a**luminate **f**errate **t**risulphate hydrate”, AFm is an acronym of “**a**luminate **f**errate **m**onosulphate hydrate”. AFt phases are formed, if three moles of sulphate are available per mole reacted C_3A. The best known AFt phase is ettringite. If one mole of sulphate is available per mole reacted C_3A only, AFm phases are formed. Like CSH phases, AFt and AFm phases are capable of incorporating trace elements in terms of crystal chemistry.

Following the hydration of Portland cement, all original clinker phases and water have been transformed into the hydrate phases of CH, $C_{1.8\text{-}2}SH$, AFt, and AFm in the ideal case. These hydrate phases form the hardened cement paste. Actually, hydration is rarely complete even after years. At the same time, an initially superficial weathering process starts after a few days already. It causes the structure and composition of the hydrate phases making up the hardened cement paste to be changed strongly. The underlying reactions are largely unknown.

Weathering of Cement-bound Construction Materials

Weathering of hardened cement paste is caused above all by the high pH value (about 12.5 – 13) developing in the interstitial water by the reaction with the hydrate phases under the exclusion of air. In contact with the atmosphere, however, the liquid films existing in and on hardened cement paste have a pH value of about 7 and, hence, act as an acid. Any contact with the outer world consequently leads to an acid attack with certain elements, in particular calcium, being dissolved selectively. During this process, the pH of the interstitial water decreases slowly. Apart from the atmosphere, also other acid sources, such as acid rain or microbiological activity, may accelerate the dissolution process.

As the acid attack usually takes places from outside, reaction velocity depends on the transport of the acid into the component. On the surface, the reaction starts immediately. If cracks or continuous pore systems exist, the reaction front rapidly moves from the outside to the inside of the component. In properly produced cement-bound materials, however, the pores are small and filled with water. This allows for a diffusion-controlled, slow transport of the acid only. Therefore, no macroscopic damage of the hardened cement paste becomes visible while using cement-bound components. Apart from the acid attack, a number of other damage mechanisms (e.g. attack by de-icing salts, sulphate-containing solutions, alkali-silica reaction) are known, which may lead to the destruction of the cement.

Following demolition, concrete components are mostly crushed in a recycling plant and subsequently utilised for earthwork and road construction or as a secondary aggregate. By crushing, new surfaces are produced, which are immediately subject to an acid attack. The small grain sizes of the crushed material shorten the diffusion length. Not completed cracks open up new diffusion paths. As a result, the selective dissolution rate of hardened cement paste is strongly accelerated.

In principle, trace elements that entered the cement during the production process are incorporated in the cement paste during hardening. However, the type of bonding may differ significantly. In case of physical inclusions, fast release is possible after demolition and recycling. In case of sorption on surfaces or crystal chemistry incorporation, stability of the respective bonds against dissolution attacks is of decisive importance. Predictions over long terms can only be made for specific scenarios.

For this purpose, the primary bonding of the corresponding trace element in the fresh cement paste must be identified first. If the phase transformations of the principal cement hydrates due to ageing and weathering are known in addition, trace element mobilisation can be described in principle for a given weathering scenario. Unfortunately, neither primary bonding of the trace elements in hardened cement paste nor phase transformations of the cement hydrates have been examined in detail so far.

Several laboratory tests described in literature serve to simulate a specific weathering scenario within a short period of time. However, transferability of the results to real conditions has not yet been confirmed.

Quality of the Analysis of Trace Elements in Solids and Solutions

In analysis, the term of trace elements generally refers to elements of less than 100 ppm concentration. Many of the analyses quoted below exceed this limit for individual elements. Hence, these elements actually represent main elements. For instance, the mean zinc content of German Portland cements amounts to about 160 ppm. Still, the term of trace element is kept for these elements so as to distinguish them from the main elements that reach concentrations in the percent range.

Nearly all assessments made below are based on trace element contents published in literature. However, quality of the data available differs considerably. A first problem is representative sampling. For silicate-bound solids an error in the range of 50% is possible and sometimes even the rule during subsequent decomposition (transfer of the solid phase to the solution). To prevent such errors, decomposition in nitric acid and hydrofluoric acid in the microwave has proved to be suitable for cement or hardened cement paste [VDZ, 2001; van der Sloot et al., 2001]. Still, the deviations observed in laboratory comparisons are considerable [van der Sloot et al., 2001]. Other decomposition methods lead to extreme errors [Schoenberger and Buchanan, 2002]. Another source of error are the analytical procedures and the equipment applied. In spite of the large errors known, the data given in literature sources often are insufficient. Sometimes, data are lacking completely.

1.3 Aim and strategy of the investigation

The aim of this project was to demonstrate the effect of different kinds of input materials, in particular of secondary fuels, secondary raw materials, interground additives, and concrete admixtures, on trace element concentrations of cement and concrete. According to the Waste Management and Recycling Act, it must be guaranteed that the use of waste as input material is proper and not harmful. For this reason, this project was additionally aimed at compiling the present knowledge on the bonding and mobilisation of trace elements in clinker, cement, and concrete.

The present study was performed by three institutes of Forschungszentrum Karlsruhe under the direction of the Institut für Technikfolgenabschätzung und Systemanalyse (ITAS, Institute for Technology Assessment and Systems Analysis). While the material flow analyses were carried out by ITAS, mineralogical investigations were run by the Institut für Technische Chemie – Bereich Wasser- und Geotechnologie (ITC – WGT, Institute for Technical Chemistry – Water Technology and Geotechnology Division). The legal part as well as the explanations concerning the measurement program have been prepared by the Institut für Technische Chemie – Zentralabteilung Technikbedingte Stoffströme (ITC-ZTS, Institute for Technical Chemistry - Department of Technology-induced Material Flow).

Compilation of a database on trace element concentrations of input materials for cement and concrete

Estimation of the trace element contents of cement and concrete is based on a database covering the type and quantity of input materials used as well as their trace element concentrations. For this, an extensive data collection is accomplished and average values as well as ranges of trace element contents are compiled for the different materials used as well as for clinker and cement.

Model calculations for trace element concentrations of cement

An extensive measurement campaign was performed by the VDZ to determine trace element concentrations of cements. However, the relevance of the individual input paths to the trace element concentration in cement cannot be gathered from these values. In order to estimate this relevance, model calculations are carried out using the database generated here. Doing this, it may be assumed that the impact of the use of secondary fuels on the trace element concentration of cement can be shown better by model calculations than by measured values, since the latter represent a snapshot only and are influenced by a set of factors. On the average, a higher trace element concentration in an input material selected inevitably causes an increase in the trace element concentrations of cement, even if this increase cannot be detected by measurements. For example, this effect may be superposed by varying trace element concentrations of the other input materials. Only when secondary input materials contain significantly higher concentrations of trace elements than primary input materials, may increased concentration values be measurable in cement.

For the model calculations two different approaches are used:

- Top-down approach
- Bottom-up approach

Within the **top-down approach** basic data are the amounts of raw materials, fuels, and interground additives used in a certain year. Taking into account the trace element concentrations of the respective input materials, average concentrations of individual trace elements in cement and information on the contribution of individual input paths result.

Since the type and amount of materials used for the manufacture of a defined amount of cement differ from plant to plant, trace element concentrations of the clinker and cement will vary from plant to plant and deviate from the mean value. Accordingly, contributions by the individual input materials will differ, too. For this reason, ranges of trace element concentrations of cement are calculated by means of a **bottom-up approach** which defines certain scenarios of combinations of input materials.

The listed trace element contents of input materials are based on an extensive compilation of data. However, these data cannot be analysed statistically. Therefore, it is impossible to check whether the mean values used for the calculations are representative. For this reason, **sensitivity calculations** are performed both in the top-down approach and in the bottom-up approach to evaluate the impact of uncertainties and fluctuations of data of trace element concentrations in the input materials on the concentration values in cement as well as on the contribution of individual input paths.

Estimation of trace element contents of concrete

In construction industry cement only is an intermediate product that is used in particular for the production of concrete. Hence, concrete also is of interest in these investigations. For this reason, concentrations of individual trace elements in concrete are calculated for four different scenarios on the basis of the calculated concentration values in cement. Again, the contribution of individual input paths is determined.

Bonding, hydration, and mobilisation of trace elements

In order to guarantee the sustainable use of cement-bound construction materials throughout the entire life cycle, the environment should not be adversely affected, especially during production, service life, recycling or disposal. Thus, conditions, mechanisms, and the corresponding rates of dissolution, which result in the mobilisation of trace elements from these materials have to be examined.

To assess the fixation and mobilisation behaviour of trace elements from cement hydrates, their chemical incorporation in unhydrous cement components is important. For this reason, chemical bonding of trace elements in main and minor constituents of Portland cement is studied more closely. It is shown that the incorporation behaviour of trace elements in Portland cement varies considerably due to variable process control and variable use of wastes in the clinker burning process. For concrete, chemical bonding and reactivity of trace elements in non-cementitious constituents are determined.

Furthermore, the hydraulic and pozzolanic reactions are described, by means of which trace elements are transferred from cement into the hardened cement paste of concrete. The information available on the incorporation of trace elements in hardened cement paste of varying age and weathering degree is presented both in a mineral-specific and in an element-specific way. It is shown which trace element fractions behave in a potentially mobile or inert manner.

Based on the data obtained, a standard weathering model for hardened cement paste is presented. Using this model, trends for the potential trace element mobilisation can be estimated in the course of the production, service life, recycling, and final disposal of concrete. Additionally, the suitability of existing test procedures for estimating the trace element release from concrete is evaluated.

Trends

This chapter briefly presents the changes in the use of raw materials and fuels in cement industry during the past years in Germany and other European countries. For Germany, the impact of these changes on the trace element content of cement is assessed additionally. Finally, further development of the use of secondary raw materials, fuels, and interground additives in Germany is discussed.

This chapter also presents the research need identified in this project. This includes proposals of measurement programs, by means of which the understanding of material flows in the clinker burning process can be improved and the contributions of individual input paths to the trace element content of cement during cement milling can be identified.

Legal bases

In Germany, the handling of wastes and their incineration are subject to the Waste Management and Recycling Act, on the one hand, and the Federal Immission Control Act with its pertinent ordinances, on the other. Relationships and current developments shall be presented.

Co-incineration of waste in the production of cement is additionally governed by directives, standards, regulations, etc. from the construction sector. To make statements with regard to the proper and unrestricted reuse as required by the Waste Management and Recycling Act, selected regulations that have to be taken into account when evaluating the product quality shall be presented.

Excursus: Emission and transfer factors

For decision support in licensing procedures, calculation processes based on material flow analysis become increasingly important when using secondary fuels in thermal processes of power plants, cement kilns, and industrial furnaces. In the German state of North Rhine-Westfalia, material flow analysis is applied to check in advance whether the permissible emission limits will be observed, if certain secondary fuels are used. For this evaluation predefined emission and transfer factors are used. Since the emission and transfer factors estimated for the same trace elements in different technical plants vary significantly, their use is subject to dispute.

2 Transfer of trace elements into cement and concrete: material flow analyses

2.1 Generation of a database

To calculate trace element concentrations of clinker, cement, and concrete as well as the contributions of individual input materials to trace element concentrations of cement and concrete, data have to be available on the kind and quantity of different input materials as well as on their trace element concentrations. To evaluate the significance of calculated values, these have to be compared with measurements. This is why data on trace element concentrations of clinker and different types of cement also have to be available.

Data on the following input materials and products were collected:

Class	**Input materials**
Primary raw materials	Limestone, marl lime, clay stone, sand, trass
Regular fuels	Hard coal, brown coal, oil coke*, oil shale
Secondary fuels	Used tyres, waste oil, scrap wood, fractions from municipal, industrial, and commercial wastes, incl. paper wastes, plastic wastes, automobile textiles, paper/plastic mixtures
Secondary raw materials	Iron ore**, materials from iron and steel works (dusts from steel works, pyrites cinder, mill scale, contaminated ore), foundry sand, ashes from burning processes, coal fly ash
Interground additives	Natural gypsum, anhydrite, gypsum from flue gas desulphurisation, fly ash, oil shale, foundry sand, trass
Intermediate and final products	Raw meal, clinker, Portland cement, blastfurnace cement
Concrete aggregates and additives	Basalt, blast-furnace slag, coal fly ash, sand, gravel

* Allocation of oil coke is not clear. Oil coke may be considered a waste material of petrol industry. In this study, oil coke was classified to be regular fuel.

** Allocation of iron ore is not clear. It may be considered both a primary and secondary raw material. In the calculation below, iron ore was considered to be a secondary raw material.

To calculate the expected range of trace element concentrations in cement, which results from the varying composition of input materials, additional information is required on reasonable combinations of input materials for cement production and on the concentration range and frequency distribution of the individual trace elements for each input material.

The search for data on trace element concentrations of the mentioned input materials for cement production, clinker, and the individual types of cement covered a large number of sources. Apart from an internet search, numerous technical journals (Zement-Kalk-Gips, Journal of Hazardous Waste, Entsorgungspraxis, Umweltpraxis, Müll und Abfall, etc.), dissertations and theses were evaluated. In addition, data collections from licensing authorities, state offices, and the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR, Federal Office for Geosciences and Raw Materials) were used. Furthermore, experts from iron and steel industry and the recycling sector were interviewed. Only a few data were supplied directly by cement works. Data on cement works were provided by the Verein Deutscher Zementwerke (VDZ, German Cement Works Association).

The database used as a basis for the following model calculations is rather extensive and comprises approximately 300 data sources. A survey of the data availability on the different input materials is given in table A1 in the annex. For a number of wastes, in particular for wastes that have been used for decades already (used tyres, waste oil), relatively few data are available only. This may be due to the fact that when first using these wastes as secondary fuels, their trace element contents were not in the centre of interest. For wastes that have been applied as fuels for a few years only, e.g. “fuels from production-specific industrial wastes” (BPG) and “substitute fuels from municipal wastes” (SBS) the data situation is rather good. Licensing of the use of these fuels requires compliance with certain trace element concentration limits. Hence, measurements have to be carried out.

Data on the constituents of the most important input material, raw meal, were mainly taken from literature, for instance, from sources of the BGR and the state offices. These institutions dispose of data collections on rocks used as raw meal constituents in cement production. Sometimes, up to 2500 individual samples had been taken. However, these data are only available in aggregated form, the individual data cannot be accessed. Also for raw meal used in clinker production plants in Germany, only aggregated data exist. Representative data on trace element concentrations including their ranges, and distributions are not available.

Data on secondary raw materials and interground additives exhibit clear deficits. Furthermore, the classes of input materials cannot be allocated clearly. For instance, coal fly ash or trass may be applied as both interground additive or raw material. A detailed list of all actually employed input materials of the class of secondary raw materials does not exist, as they represent a rather heterogeneous set of numerous individual materials.

Comparison of the trace element concentrations given in various literature sources turned out to be rather problematic. In some cases, various ranges are given. In other cases, mean values, 10-percentile, 50-percentile, or 90-percentile values are available. Moreover, the number of trace elements considered varies considerably. Within the framework of the present study, however, quality of the analyses quoted in literature was not checked.

As far as cements are concerned, the concentration values of more than 400 random samples taken for the quality control of German normal cements, as published by the VDZ in 2000 [VDZ, 2000], represent the most important data apart from other literature information. According to the VDZ, these measured values are based on a representative selection of all cements produced in 1998.

For each input material as well as for intermediate and final products of cement production, minimum, maximum, and average concentration values were determined from the data collected for each individual element considering each individual data source. A weighted average was calculated from these average values, with the scope of sampling being taken into account to the extent possible.

The trace element concentrations calculated from the literature data were then compared with trace element concentrations of raw meal components, regular fuels, and used tyres, which were published recently by the VDZ [Locher, 2000] as well as with an extensive data collection made by the “Bundesgütegemeinschaft Sekundärbrennstoffe” (BGS, Federal Association for the Quality of Secondary Fuels) [Flamme and Gallenkemper, 2001]. This comparison revealed that the average trace element concentrations of raw meal components and regular fuels given here lie in the upper range of those given by the VDZ. For some elements the concentrations even exceed the maximum values given by the VDZ. When performing model calculations with these data, the contribution of raw meal components and regular fuels to the total trace element concentration in cement may therefore be overestimated, while the contribution by other input materials, such as secondary fuels, may be underestimated.

Trace element concentrations of fuels from production-specific wastes (BPG) and substitute fuels from municipal wastes (SBS), which are compiled in this study, are based on a large number of analyses. For calculation purposes in this study these two waste fractions (BPG and SBS) are combined to one fraction called “fractions from municipal, commercial and industrial waste”. Minimum, maximum, and average values derived from these data correspond to the minimum, maximum, and average data given by the BGS for these waste categories [Flamme and Gallenkemper, 2001] (s. also table 40 in the section “Legal bases”).

Input materials from iron and steel industry are characterised by a strong heterogeneity and a large range of trace element concentrations. As it may be assumed that materials (especially dusts) with high trace element concentrations are not used in the production of cement, average minimum values derived from the literature data were used for model calculations rather than average values (s. table A2 in the annex, footnote 1). For the calculation of these average minimum values, highly loaded dusts, ores, etc. are not taken into consideration, since it may be assumed again that these materials are not used as input materials for the production of cement.

Comparison of the target values specified for trace element concentrations in wastes by BUWAL [BUWAL, 1998] with values given in the present study reveals that the latter values remain below the target values. If the target values are exceeded by the data compiled here for a certain type of waste, use of this type of waste is permitted by a “positive list” of BUWAL. This positive list is an annex of the regulation, listing wastes that may be “disposed of” in cement works, although target values are exceeded. The list also contains limit values. However, these are on a higher level than the target values. Trace element concentrations given in the present study all remain below limit values of the positive list except for coal fly ash.

The average values and ranges of trace element concentrations of the input materials, intermediate and final products as compiled by this study are listed in table A2 in the annex.

2.2 Average input of trace elements in cement: the top-down approach

2.2.1 Methodology of the top-down approach

The top-down approach is used to compute average trace element concentrations of cement and the contributions of individual input paths to the total content. This approach does not consider individual plants, but is based on the total cement production of a certain year.

To estimate the trace element concentrations of various cements and the contributions of primary and secondary input materials to this concentration, the following data sources were applied:

- Trace element concentrations of all input materials (table A2 in the annex)
- Amounts of primary and secondary raw materials, fuels, and interground additives used in 1999 [VDZ, 2001]
- Statistics on domestic sales of certain types of cement for 1999 [VDZ, 2001]
- Statistics on the total cement production in Germany [BDZ, 1999]
- Data on the main and minor constituents of normal cements according to DIN EN 197-1

Trace element concentrations of input materials

Table A2 (annex) presents the average values and ranges of trace element concentrations of input materials as determined from various sources within the framework of this study. The input materials considered were selected according to the input materials listed in the environmental data of VDZ [VDZ, 2001]. Calculations using the top-down approach were based on the average trace element concentrations only. Hence, use of this calculation approach only allows for the assessment of average trace element concentrations of clinker and individual types of cement, a calculation of ranges is impossible (s.a. sensitivity calculation, section 2.3).

Amounts of input materials used annually

The amounts of materials used for cement production in 1999 were taken from the environmental data as provided by German cement industry [VDZ, 2001]. There, the input materials are divided into groups (Ca group, Si group, Si-Al group, Si-Al-Ca group, etc.) rather than into raw materials, fuels, and interground additives. To distinguish between the amounts of raw materials and interground additives, the production statistics as explained in detail below and the EU standard [DIN EN 197-1] were used. With the aid of the production statistics and the EU standard, composition of the individual types of cement was determined. From this, the amounts of interground additives needed to produce the various types of cement could be derived. The amount of interground additives not required for cement milling was assigned to clinker production. The amounts of input materials used for clinker production and cement milling are given in table A3 in the annex.

Statistics on the individual types of cement

The production statistics published in the VDZ "environmental data" only indicate the domestic sales of the individual types of cement in addition to annual clinker production. No data are available on the amounts of the individual types of cement produced. However, the report "Zahlen und Fakten 1998/1999" (Data and Facts, 1998/1999) by the Federal Association of German Cement Industry (1999) contains data on annual cement production without individual types of cement being distinguished [BDZ, 1999]. Taking into account the shares of the individual types of cement in the domestic sales (VDZ Produktionsstatistik), the individual types of cement produced were then estimated from total cement production (BDZ data). A survey of the amounts produced as derived from both literature sources is given in table A4 in the annex.

Major and minor constituents of the types of cement

Based on the amounts of clinker and cement used and taking into account the European cement standard [DIN EN 197-1] as well as the amounts of input materials used according to the VDZ, the constituents of the individual types of cement were identified (table 2).

Table 2: Survey of cement types and their major and minor constituents (without gypsum) used for the calculations.

Type	Denomination	Major constituents	Minor constituents
CEM I	Portland cement	99.1% Clinker	0.2% Coal fly ash, 0.5% Oil shale 0.2% Pozzolana
CEM II	Slag cement	65% Clinker, 30% Slag	0.5% Coal fly ash 4.5% limestone
CEM II	Limestone cement	65% Clinker, 34% Limestone	1% Coal fly ash
CEM II	Shale cement	65% Clinker, 35% Oil shale	
CEM II	Pozzolanic cement	65% Clinker, 34% Pozzolana	1% Coal fly ash
CEM III	Blastfurnace cement	19% Clinker, 76% blast-furnace slag	5% Limestone

Having a look at this survey of cement types, it must be taken into account that the list published by the VDZ on amounts of input materials used does not include any data on electrostatic precipitator ashes and bypass dusts arising in the process. It was assumed that these dusts were not milled into the cement as minor constituents, but represented major constituents of clinker. In the table above, “clinker”, hence, is a mixture of clinker granules, bypass dusts, and electrostatic precipitator ashes.

According to the European cement standard [DIN EN 197-1, 2001], calcium sulphate and, if applicable, cement additives are added to these major and minor constituents. Calcium sulphate may be gypsum ($CaSO_4$ x 2 H_2O), hemihydrate ($CaSO_4$ x ½ H_2O), anhydrite ($CaSO_4$) or a mixture of these substances. The amounts of gypsum and anhydrite used were derived from the amounts used as given by VDZ. Accordingly, 5% of calcium sulphates each were assigned to the individual types of cement for the calculations. Cement additives were not considered by the calculation.

2.2.2 Trace element concentrations of raw meal, clinker, and cement

Following the evaluation of the data collection, 13 trace elements were selected for further investigation: antimony, arsenic, lead, cadmium, chromium, cobalt, copper, manganese, nickel, thallium, tin, vanadium, and zinc. Due to lacking data, beryllium, selenium, and tellurium were excluded from the calculation. Although a number of data exist on mercury, the amount transferred into clinker or cement can hardly be determined due to its high volatility.

In 2000, the VDZ published data on trace element concentrations of German normal cements. These data had been obtained during the quality control of these cements and covered about 400 samples with 17 different trace elements [VDZ, 2000]. According to the information supplied by the VDZ, these data are representative of all different types of cement produced in 1998. To compare trace element concentrations calculated for the cements with the VDZ values, an average trace element concentration for a theoretical "mixed cement" was derived taking into account the shares of the different types of cement in total production. This mixed cement has the following composition:

"Mixed cement": Portland cement 66%, blastfurnace cement 14%, slag cement 13%
limestone cement 6%, shale cement 1%, pozzolanic cement <1%

Based on the data described, trace element concentrations of raw meal, clinker, various types of cement, and of the theoretical mixed cement were calculated and, if available, compared with literature values (table 3).

As evident from table 3, the calculated values are in the range of the values quoted in literature. As far as raw meal is concerned, arsenic, manganese, antimony, and zinc show larger deviations between the calculated average values and the average values given in literature. However, the concentration values lie in the range of the literature values. For Portland cement the calculated trace element concentrations of arsenic, antimony, and zinc do not differ from the values published.

Strong increase of the concentration of cadmium, antimony, and zinc from raw meal to clinker is clearly visible. It exceeds the increase in concentration resulting from CO_2 discharge and the associated mass loss. This increase is assumed to be caused largely by fuels. As will be confirmed later when analysing the input paths, concentration increase above all of antimony and zinc is caused by secondary fuels (see figure 4, figure 7, table A5).

Table 3: **Trace element concentrations (in ppm) of raw meal, clinker, and various types of cement. Comparison of average values calculated using the "top-down approach" with the range of data taken from literature. Min = minimum value; Max = maximum value; AV = average values; n.a. = not available.**

		As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sb	Sn	Tl	V	Zn
Raw meal "top-down"	AV	**5**	**0.3**	**5**	**25**	**21**	**480**	**22**	**20**	**2**	**4.3**	**0.4**	**32**	**53**
Raw meal "literature"	Min	2	0.03	3	23	5	50	12	1.7	0.1	2	0.1	6	10
	Max	28	1.1	14	59	19	500	38	98	2	10	12	120	108
	AV	**9**	**0.3**	**7**	**30**	**14**	**236**	**20**	**14**	**1**	**3**	**0.5**	**37**	**34**
Clinker "top-down"*	AV	**9**	**0.8**	**11**	**48**	**40**	**864**	**44**	**41**	**5**	**8.5**	**0.9**	**68**	**159**
Clinker "literature"	Min	2	0.01	6	10	5	218	10	1	0.1	1	0.01	10	29
	Max	87	4	48	422	136	526	397	105	17	36	10	136	600
	AV	**9**	**1**	**13**	**66**	**38**	**400**	**38**	**24**	**5**	**13**	**0.5**	**57**	**113**
Portland cement "top-down"	AV	**9**	**0.8**	**10**	**46**	**39**	**816**	**42**	**40**	**5**	**8.0**	**0.9**	**66**	**153**
Portland cement "literature"	Min	2	0.03	3	25	14	107	14	5	0.5	1	0.02	15	21
	Max	117	6	21	712	98	3901	97	254	18	14	4.1	144	679
	AV	**8**	**0.6**	**11**	**68**	**38**	**606**	**45**	**27**	**5**	**3**	**0.6**	**74**	**164**
Blastfurnace cement "top-down"	AV	**3**	**0.7**	**5**	**28**	**12**	**2707**	**13**	**13**	**2**	**5.3**	**0.7**	**36**	**59**
Blastfurnace cement "literature"	Min	0.8	0.1	0,2	19	5	n.a.	4	1	n.a.	n.a.	n.a.	62	5
	Max	15	1	18	246	160	n.a.	53	136	n.a.	n.a.	n.a.	444	245
	AV	**6**	**0.5**	**6**	**50**	**13**	**n.a.**	**17**	**13**	**5**	**n.a.**	**0.5**	**113**	**122**
Slag cement "top-down"	AV	**7**	**0.7**	**8**	**39**	**29**	**1561**	**31**	**30**	**4**	**6.9**	**0.8**	**55**	**115**
Pozzolanic cement "top-down"	AV	**7**	**0.7**	**7**	**46**	**28**	**545**	**31**	**43**	**3**	**5.4**	**0.9**	**47**	**144**
Shale cement "top-down"	AV	**9**	**1.0**	**7**	**50**	**46**	**540**	**28**	**39**	**3**	**5.3**	**1.2**	**43**	**163**
Limestone cement "top-down"	AV	**8**	**0.6**	**8**	**36**	**32**	**706**	**36**	**34**	**4**	**6.7**	**0.7**	**55**	**115**
"Mixed cement" "top-down"	AV	**8**	**0.7**	**9**	**42**	**34**	**1164**	**36**	**35**	**4**	**7.4**	**0.8**	**59**	**133**
Normal cement VDZ [VDZ, 2000]	10-Perc	1.6	0.1	4	23	9	255	13	10	1	n.a.	n.a.	30	48
	90-Perc	13.6	0.8	17	59	43	1268	39	48	15	n.a.	n.a.	93	291
	AV	**6.8**	**0.4**	**10**	**40**	**25**	**680**	**24**	**27**	**6**	**4.6**	**n.a.**	**56**	**140**

* The trace element concentration of clinker is overestimated since some trace elements, especially volatile ones, will partially be trapped in filter dusts which is not considered in the calculation. However, after adding filter dusts to the cement the balance is regarded to be correct again. This applies especially for elements such as cadmium, lead, and thallium.

It can also be noted that the concentrations in blastfurnace cement are smaller than in Portland cement.

For blastfurnace cement hardly any data are available in literature. This limits the comparability of calculated values. No data were available on the trace element concentrations of slag cement, pozzolanic cement, oil shale cement or limestone cement. Trace element concentrations of the "mixed cement" are in good agreement with the values measured by the VDZ.

2.2.3 Identification of the input pathways of trace elements into cement

Based on the trace element concentrations of input materials, trace element concentrations for cement and clinker were calculated. These values show a good agreement with data from literature and with values measured by the VDZ. Therefore, it may be assumed that the calculations also give reliable information about the contribution of different types of input materials, such as secondary fuels, secondary raw materials, and interground additives, to the total trace element concentration of cement. In the following sections, the contributions of individual input materials to total trace element concentrations in cement will be presented. Studies were performed for Portland cement, as it is the most frequently used cement in Germany and exhibits the highest concentrations of most trace elements according to the calculations. In addition, the input pathways into "mixed cement" were estimated.

For Portland cement the following classes of input materials can be distinguished:

Class	**Input materials**
Primary raw materials	Limestone, marl lime, clay stone, sand, trass
Regular fuels	Hard coal, brown coal, oil coke*, oil shale
Secondary fuels	Used tyres, waste oil, scrap wood, fractions from municipal, industrial, and commercial wastes
Secondary raw materials	Iron ore**, materials from iron and steel works (dusts from steel works, pyrites cinder, mill scale, contaminated ore), foundry sand, ashes from burning processes, coal fly ash
Interground additives ***	Natural gypsum, anhydrite, gypsum from flue gas desulphurisation, coal fly ash, oil shale, trass

* Allocation of oil coke is not clear. Oil coke may be considered a waste material of petrol industry. In this study, oil coke was classified to be regular fuel.

** Allocation of iron ore is not clear. It may be considered both a primary and secondary raw material. In the calculation below, iron ore was considered to be a secondary raw material.

*** For calculations regarding the "mixed cement" additionally to natural gypsum, anhydrite, gypsum from flue gas desulphurisation, coal fly ash, oil shale, and trass also blast-furnace slag is considered within the input path "interground additives".

The contributions of individual classes of input materials (in %) to total trace element concentrations of Portland cement and "mixed cement" are outlined in table A5 (annex). As expected, the primary raw materials represent the most important, but not only major input path for all trace elements. Also secondary input materials contribute to the trace element content of cement. Their share, however, differs from trace element to trace element. Based on the distribution pattern of the trace element input for the different classes of input materials into Portland cement, four categories can be distinguished (table 4).

Table 4: **Distribution of trace element input into Portland cement to various input pathways. Depending on their pattern of distribution, trace elements can be divided into four categories.**

Category	Description		Trace elements
Category I	Amount of trace elements introduced by primary raw materials < 55 %		**Cd** **Cu** **Zn**
Category IIa	Amount of trace elements introduced by primary raw materials between 60 - 80 %; input by fuels dominating in comparison to input by secondary raw materials	Introduction mainly by primary fuels	**Ni** **V**
Category IIb		Introduction mainly by secondary fuels	**Sb** **Tl**
Category III	Amount of trace elements introduced by primary raw materials around 70 %; input by secondary raw materials dominating in comparison to input by fuels		**Co** **Cr**
Category IV	Amount of trace elements introduced by primary raw materials around 75 %; input by fuels and secondary raw materials relatively evenly distributed		**As** **Pb** **Sn**

Two representatives each were taken from the categories I, II, III, and IV. For these elements the individual input paths are illustrated in the following figures, based on the results given in table A5 (annex). Table 5 also shows which input material plays an important role for the input of various trace elements into cement via a certain input path.

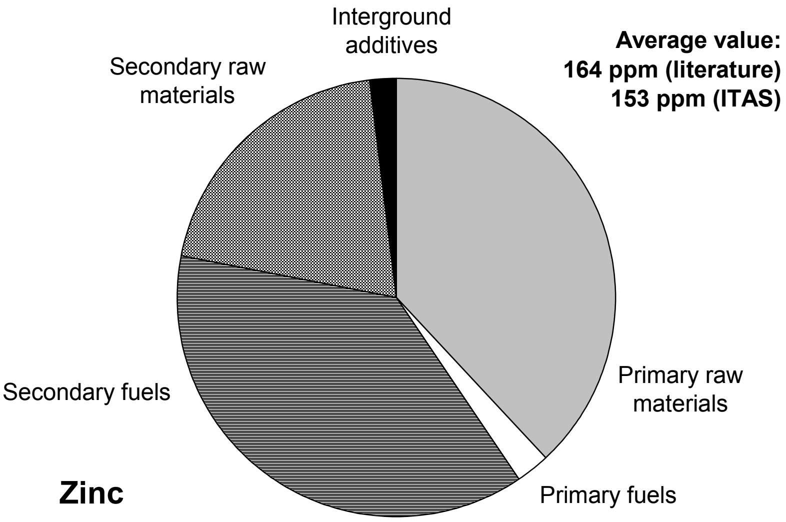


Figure 4: **Category I; relative shares of the individual input paths in the zinc content of Portland cement.**

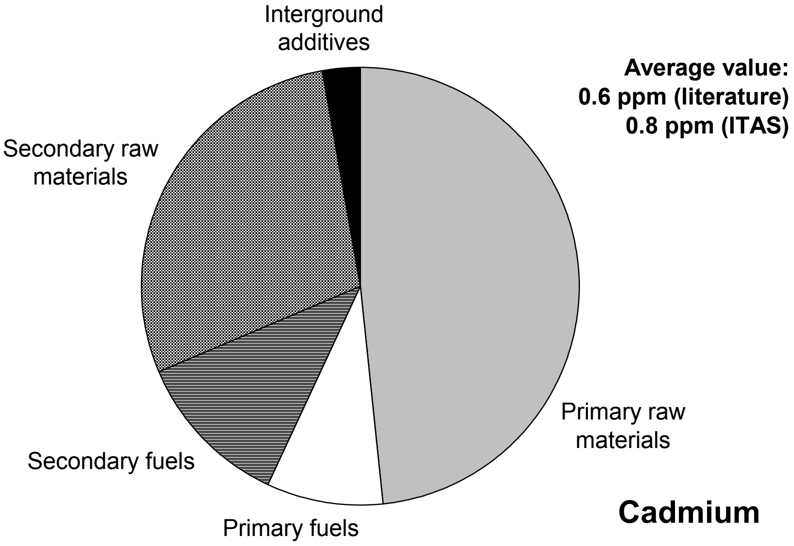


Figure 5: **Category I; relative shares of the individual input paths in the cadmium content of Portland cement.**

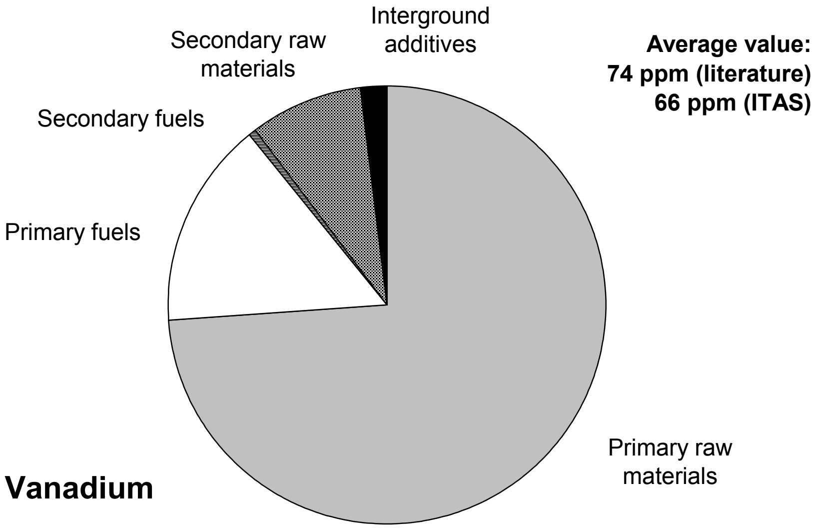


Figure 6: **Category II; relative shares of the individual input paths in the vanadium content of Portland cement.**

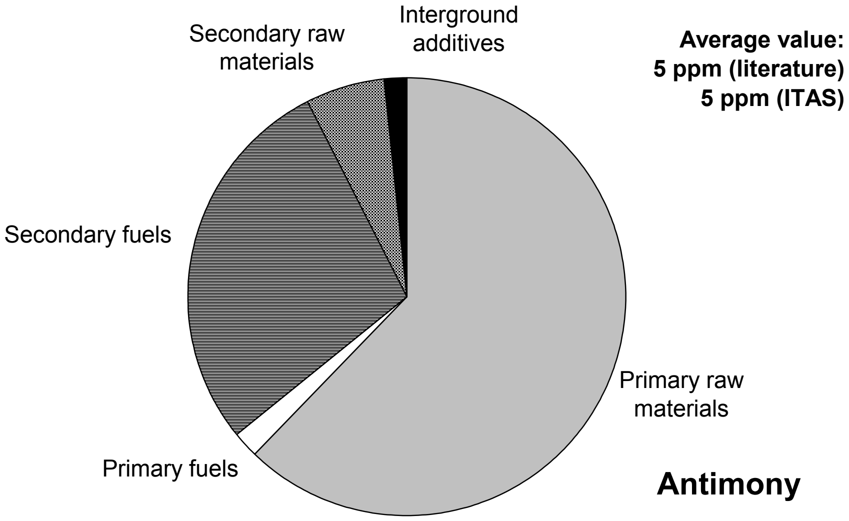


Figure 7: **Category II; relative shares of the individual input paths in the antimony content of Portland cement.**

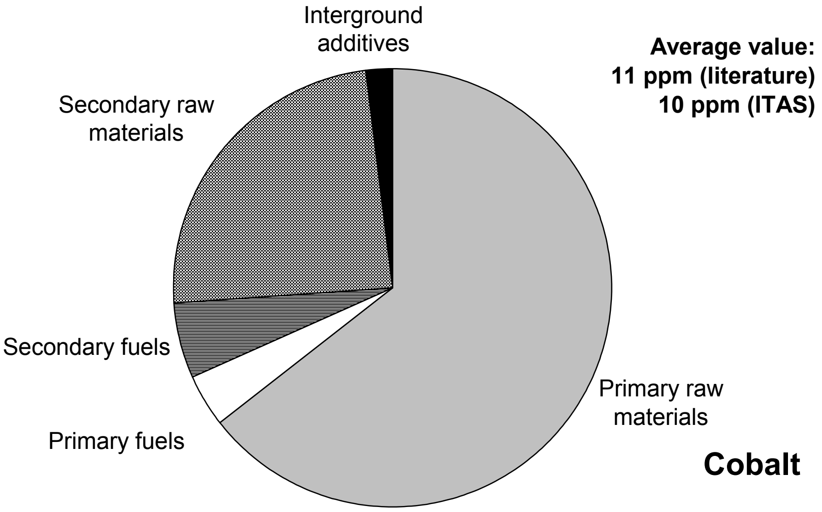


Figure 8: **Category III; relative shares of the individual input paths in the cobalt content of Portland cement.**

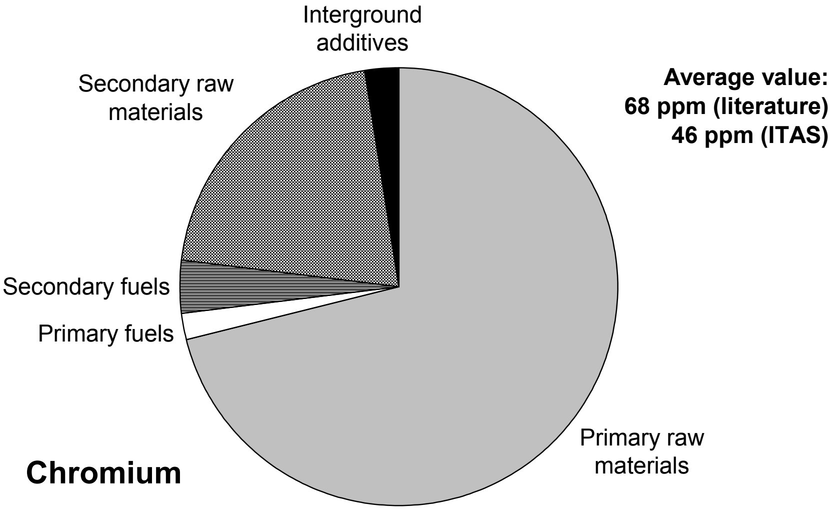


Figure 9: **Category III; relative shares of the individual input paths in the chromium content of Portland cement.**

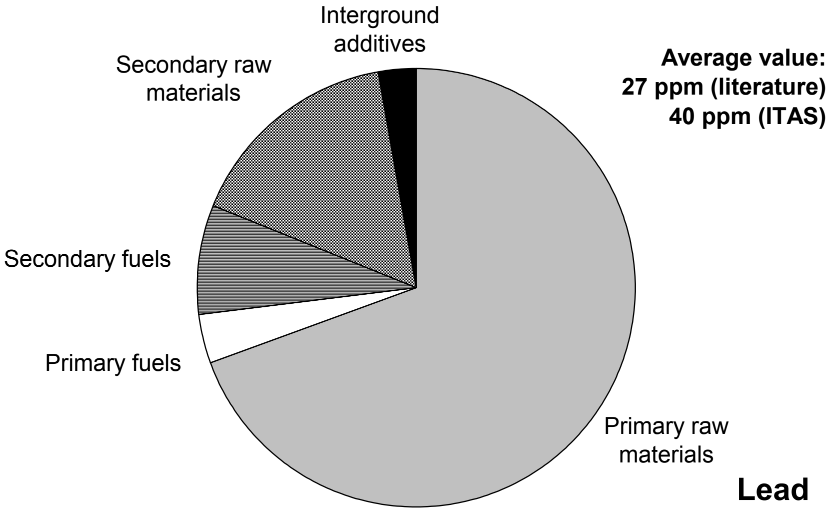


Figure 10: **Category IV; relative shares of the individual input paths in the lead content of Portland cement.**

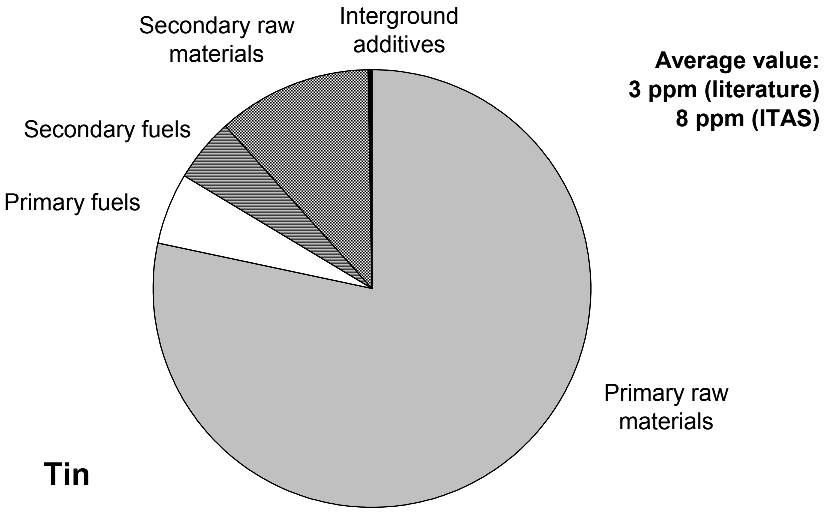


Figure 11: **Category IV; relative shares of the individual input paths in the tin content of Portland cement.**

The following conclusions can be drawn from the figures above and table 5:

For zinc and cadmium (category I) primary raw materials contribute less than 50% to the total trace element concentrations in cement. In addition, raw materials from iron and steel industry as well as secondary fuels, such as used tyres, waste oil, and fractions of commercial, municipal and industrial wastes, are important input materials.

Table 5: **Input materials representing a relevant input pathway into Portland cement apart from primary raw materials. The order reflects their importance.**

	Regular fuels	Secondary fuels	Secondary raw materials
As			Coal fly ash; iron and steel industry
Cd		Used tyres; fractions of municipal, commercial and industrial wastes	Iron and steel industry
Co		Used tyres	Iron and steel industry; iron ore; coal fly ash; foundry sand
Cr		Used tyres	Iron and steel industry; iron ore; ashes from burning processes
Cu		Fractions of municipal, commercial and industrial wastes	Iron and steel industry; iron ore; coal fly ash
Ni	Oil coke		Iron and steel industry; coal fly ash; iron ore
Pb		Used tyres, waste oil	Iron and steel industry; coal fly ash; iron ore
Sb		Used tyres; fractions of municipal, commercial and industrial wastes	
Sn			Iron and steel industry
Tl		Used tyres	Coal fly ash
V	Oil coke		Coal fly ash
Zn		Used tyres, waste oil	Iron and steel industry; iron ore

For antimony and vanadium (category II) primary raw materials contribute 62% and 74%, respectively, to the total trace element concentration in cement. Apart from raw materials, fuels are of importance. For antimony, secondary fuels, such as used tyres and fractions of municipal, commercial and industrial wastes, are relevant, while the regular fuel oil coke is an important input material for vanadium.

Cobalt and chromium belong to category III. Apart from primary raw materials, secondary raw materials are of importance. Mainly substitutes from iron and steel industry and coal fly ashes contribute to the total cobalt concentration in cement. For chromium substitutes from iron and steel industry as well as ashes from burning processes are of importance.

Lead and tin (category IV) are almost equally introduced by fuels and by secondary raw materials. Among the latter, substitutes from iron and steel industry are of particular relevance. For lead also coal fly ash plays a role.

Manganese was not represented, as it assumes a special position. 94% of manganese input occurs via primary raw materials. Input via other sources can be neglected. The four categories presented for Portland cement can also be applied to the distribution of trace element input into “mixed cement”. However, interground additives have a stronger effect, while input via other paths decreases accordingly. As these distributions are rather similar, they are not illustrated in further detail. However, the percentage shares of the individual input paths in the total trace element content of “mixed cement” are listed in table A5 in the annex. The effect of the interground additives due to an increased input via granulated blast-furnace slag is particularly noticeable for the elements cadmium, chromium, manganese, tin, thallium, and vanadium.

To correctly assess the results presented in this section, the following aspects should be taken into consideration:

Among others, the contributions of individual input paths to trace element concentration of the cement were calculated. These calculations were based on the amounts of raw materials, fuels, and interground additives used in 1999. A different composition of input materials may well result in other contributions of the individual input paths without the absolute content of trace elements in the cement being affected significantly. This means that the trace element concentration of cement does not necessarily have to decrease when doing without secondary raw materials or secondary fuels, even if these input materials have contributed considerably to the total concentration of certain elements in cement.

2.3 Sensitivity analysis of trace element inputs. Determination of the ranges of contribution of different input pathways

2.3.1 Procedure

In the previous section, relevance of the different input paths to trace element concentration in cement was determined among others. Dependence of the results obtained on the data used with regard to the trace element concentrations of the input materials shall now be investigated in more detail by means of sensitivity analyses.

To carry out such sensitivity analyses, information on the range as well as on the frequency distribution of the concentrations in input materials must be available. As mentioned when presenting the database on trace element concentrations of input materials, however, this unfortunately is not the case. This also applies to raw meal that represents the most important input material in terms of the amount.

Within the framework of quality control of German normal cements, however, more than 400 samples were analysed for their content of each of 17 different trace elements. The resulting average and individual values were published and represented graphically in the VDZ environmental report. Table 6 shows the average values published. Figures 12 and 13 present graphic representations of the cobalt and antimony measurements by way of example.

The only possibility of accomplishing such sensitivity calculations consists in assuming that for each individual element the frequency distribution of the concentration values in the input material corresponds to that in cement. From the VDZ measured values, distribution functions were determined for each individual element and applied to the different input materials.

Table 6: Average trace element concentrations of normal cements [VDZ, 2000].

Trace element	Number of samples	Average value (ppm)	Number of samples below detection limit
Arsenic	417	6.8	20
Beryllium	417	0.7	1
Cadmium	417	0.4	26
Cobalt	418	10	0
Chromium	418	40	0
Copper	417	25	0
Mercury	416	0.07	123
Manganese	418	680	0
Nickel	418	24	0
Lead	418	27	0
Antimony	414	6	61
Selenium	417	n.b.	301
Tellurium	418	n.b.	418
Thallium	418	n.b.	372
Vanadium	418	56	0
Zinc	418	140	0
Tin	411	4.6	29

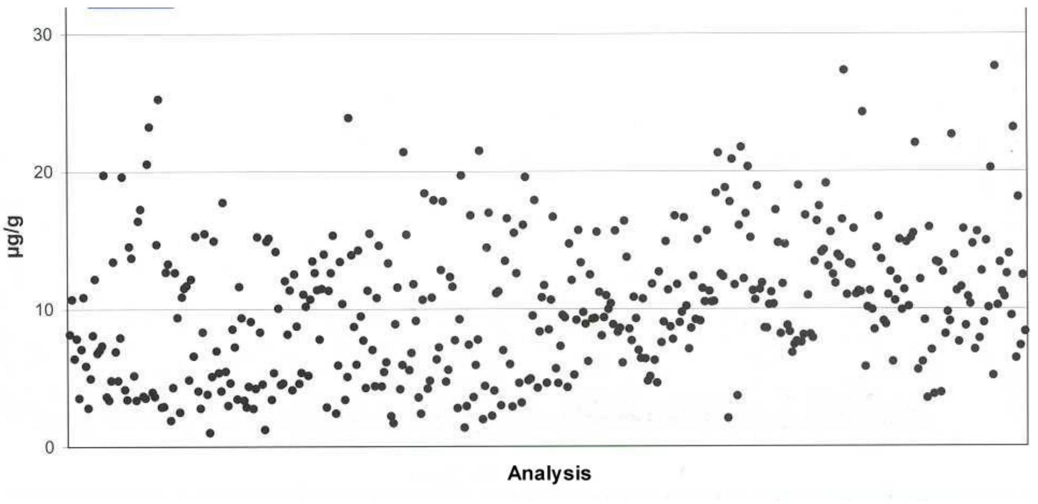


Figure 12: **Cobalt concentrations measured in the normal cements [VDZ, 2000].**

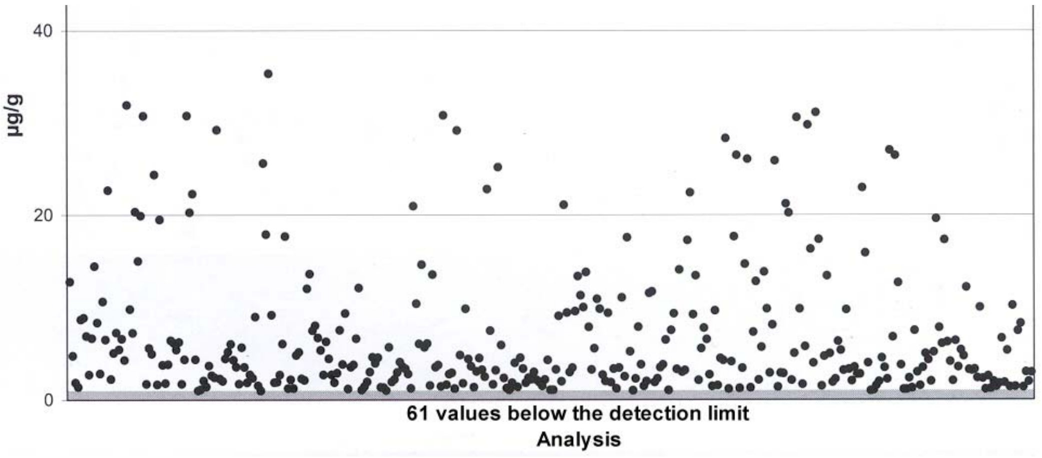


Figure 13: **Antimony concentration measured in the normal cements [VDZ, 2000].**

2.3.2 Density function and frequency distribution of selected trace element concentrations in cement

As no individual measurement data were available for the elements considered, the graphic representations of the trace element concentrations of normal cements as given in the VDZ environmental report had to be scanned. The digitised data were then evaluated. As for many elements, a multitude of measurement points is located very close to each other and it is hardly possible to clearly separate these points during digitisation, agreement of the digitised points with the given number of measurement values was checked. Since the average value calculated from the digitised measurements always was in good agreement with the average value given by the VDZ, it may be assumed that the individual measurement values were recorded correctly.

The ranges of trace element concentrations in cement differ considerably for the individual elements. For example, the average value for cadmium amounts to 0.4 ppm, while the manganese average reaches 680 ppm. For a comparative representation of the ranges of values measured, normalisation was required for the individual trace elements. This was done by dividing all concentration values of a trace element considered by the respective average value. The resulting concentration values were mostly in the range from > 0 to 3.

Subsequently, the values ordered in size were approximated by distribution functions. In all cases, sufficient accuracy was achieved by means of the gamma distribution. Figure 14 shows the density functions for zinc, arsenic, tin, manganese, and cadmium. These six elements exhibit nearly the same distribution with most of the values reaching about half of the average value.

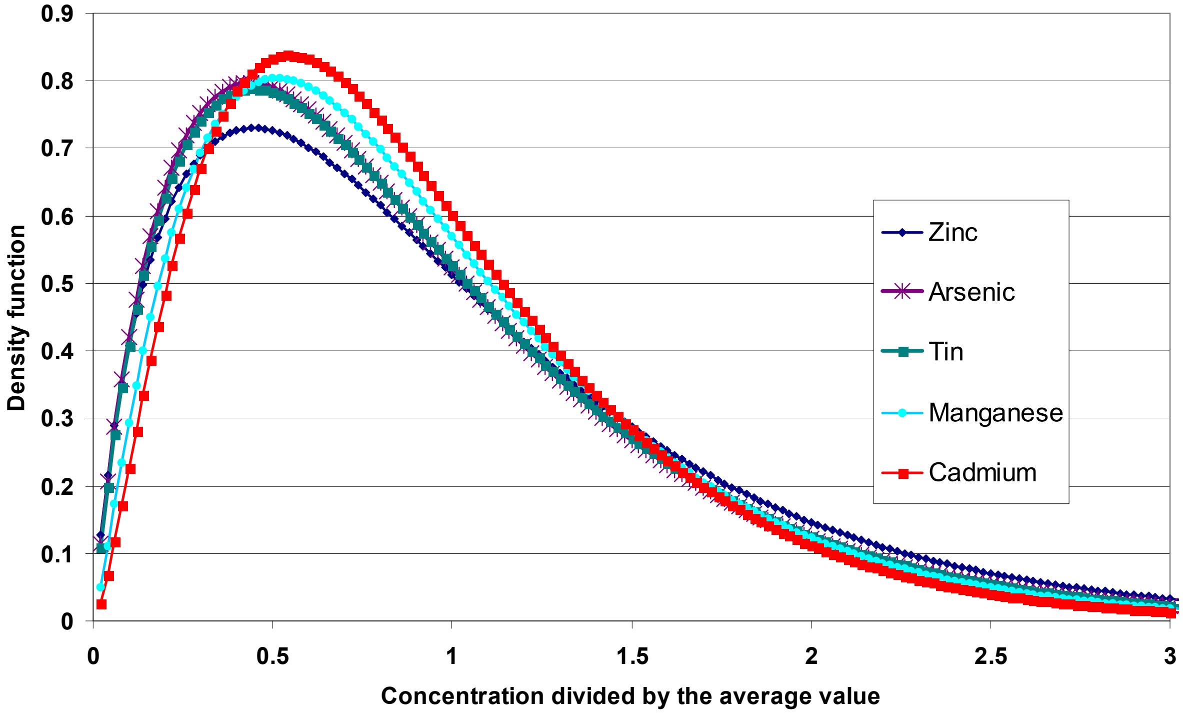


Figure 14: **Probability density calculated for concentration values of selected trace elements in normal cements, based on VDZ measurements [VDZ, 2000].**

Figure 15 shows the probability density calculated for chromium, vanadium, and nickel. Also these three elements exhibit a similar distribution with most of the values amounting to about 0.8. Compared to the values presented in figure 14, the distribution of concentration values is far more narrow, i.e. the probability of occurrence of values far above or far below the averages is smaller.

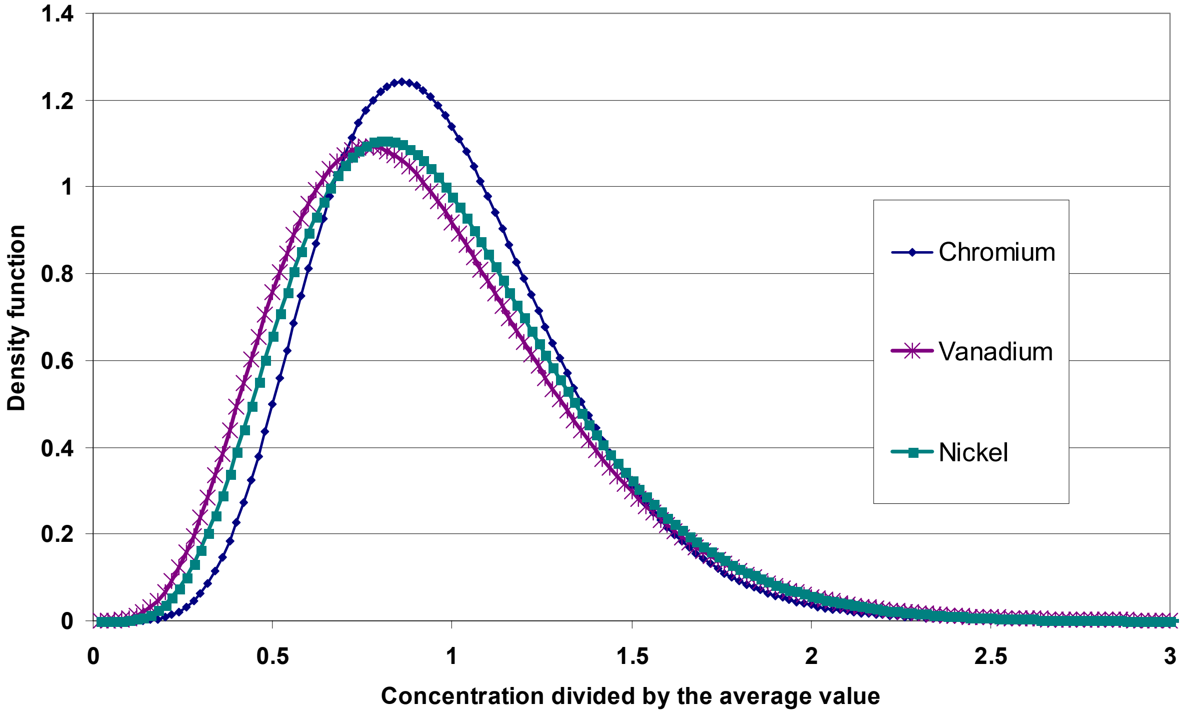


Figure 15: Probability density calculated for concentration values of selected trace elements in normal cements, based on VDZ measurements [VDZ, 2000].

Another group of elements (cobalt, lead, and copper) is represented in figure 16. Here, most of the values are in the range of 0.6 to 0.7. Again, the range of values is far more narrow than for the elements represented in figure 14.

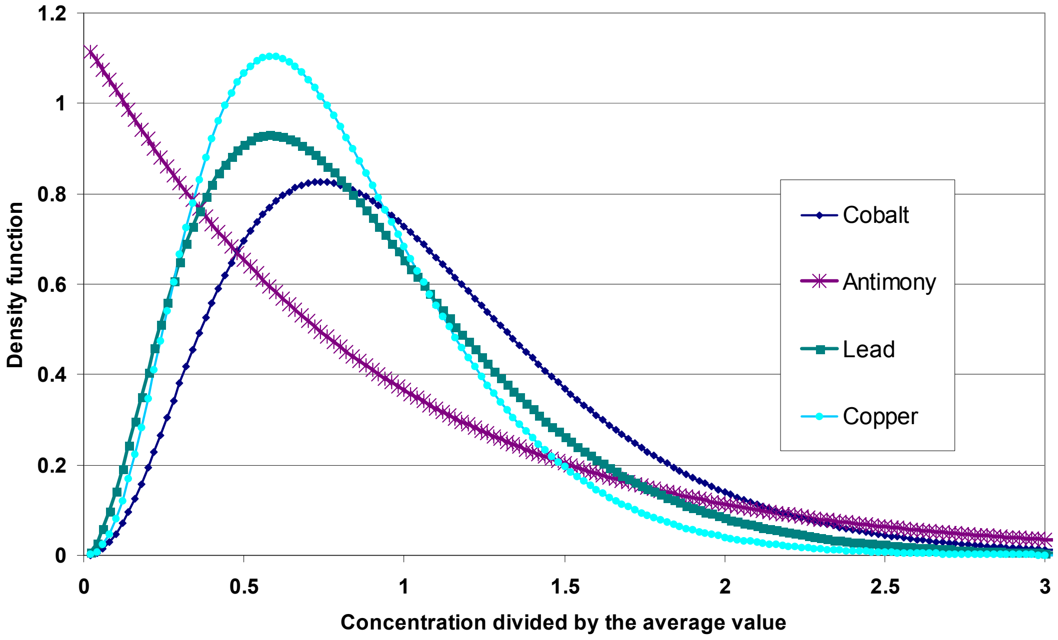


Figure 16: Probability density calculated for concentration values of selected trace elements in normal cements, based on VDZ measurements [VDZ, 2000].

A completely different behaviour is shown by antimony which is also represented in figure 16. Due to the large number of measurements below the detection limit, the probability of small antimony concentration values is rather high. Then, however, probability decreases continuously.

No distribution function could be derived for thallium, as most of the values measured in cement were found to be below the detection limit.

2.3.3 Methodological approach to performing a sensitivity analysis

From the trace element concentrations of normal cement measured by the VDZ, distribution functions were determined for the individual trace elements and the thus obtained distributions were applied to the input materials. Analyses of the distributions of trace elements in cement reveal similar patterns. Accordingly, the trace elements may be divided into the following four categories:

Category I:	As, Cd, Mn, Sn, Zn (see figure 14)
Category II:	Co, Cu, Pb (see figure 16)
Category III:	Cr, Ni, V (see figure 15)
Category IV:	Sb (see figure 16)

To calculate the distribution of concentration values of the individual elements in cement, it was proceeded as follows:

For each input material and for each element, 500 samples were generated. Additional studies with up to 2000 samples had no influence on the results of the sensitivity analyses. The individual values of the samples thus reflect the distributions that are characteristic of categories I through IV, with the average values corresponding to the average values of the input materials given in table A2 in the annex.

The minimum and maximum values generated from the samples partly are below or above the minimum and maximum values taken from literature. If, however, the smallest 10% and the largest 10% of the values are not taken into consideration, the concentration values are found to lie in the range quoted in literature. Hence, the concentration ranges given in literature for the input materials are covered well by the distribution functions selected.

Taking into account the kinds and amounts of input materials collected for the top-down calculations (see table A3 in the annex), the distribution of trace element concentrations in cement as well as the range of the shares of each input material in the total trace element concentration can be calculated from the individual sample values.

The distinction of primary and secondary raw materials, fuels, and interground additives, which is necessary to estimate the input paths, corresponded to the distinction made in the top-down approach. As additional interground additive, granulated blast-furnace slag was considered in the calculations for blastfurnace cement.

2.3.4 Contributions of individual input paths to the trace element concentration of Portland cement and blastfurnace cement

Sensitivity calculation is limited to the two most important cement types, Portland cement and blastfurnace cement. To represent the trace element concentration ranges of the cements, the range between the 10-percentile and 90-percentile values was used in order to exclude extreme values of low probability. Based on these calculations, tables 7 and 8 show the shares of each individual class of input materials to the total trace element concentration of Portland cement and blastfurnace cement.

The sensitivity calculations show that the importance of the different classes of input materials remains largely unchanged as compared to the top-down calculations based on average values. For ***Portland cement*** this particularly applies to the elements cadmium, antimony, and zinc. For these elements secondary fuels and secondary raw materials contribute significantly to the total trace element concentration in cement even when taking into consideration the possible ranges of trace element concentrations in input materials.

By comparing the ranges of fluctuation, differences of the relative shares of the individual input paths partly become less noticeable. While for cadmium the average share of secondary raw materials is much higher than the average share of secondary fuels, sensitivity calculations reveal that the share of secondary raw materials does not exceed that of secondary fuels in any case. Moreover, secondary fuels do not always reach higher shares than primary fuels. In the case of lead, the ranges of contributions from secondary fuels and secondary raw materials also overlap.

The results of the sensitivity calculations for ***blastfurnace cement*** show that when taking into consideration the possible ranges of concentration values in input materials, interground additives are most important to all elements except for arsenic, copper, nickel, and lead. For these elements contributions from interground additives are approximately as high as from primary raw materials. Secondary fuels are relevant to antimony and zinc concentrations only.

The influence of secondary raw materials is of relevance to several elements, e.g. copper and zinc, and less distinct for arsenic, cadmium, cobalt, and lead. Vanadium concentration in blastfurnace cement is influenced by regular fuels, in particular oil coke.

Table 7: **Range of the shares of individual input materials groups in the total trace element concentration of Portland cement, calculated by sensitivity analysis. Values given in percent.**

		share in total content				
		Prim. RM	Prim. F	Sec. F	Sec. RM	Interg. Addit.
Arsenic	10Perc	65	2	0	7	1
	90Perc	87	9	1	24	5
	AV	77	5	1	15	3
Cadmium	10Perc	29	4	6	15	1
	90Perc	66	15	21	45	3
	AV	48	9	13	29	2
Cobalt	10Perc	54	2	2	17	1
	90Perc	76	7	6	36	3
	AV	65	4	3	25	2
Chromium	10Perc	64	2	2	15	1
	90Perc	78	3	5	27	2
	AV	71	2	4	21	2
Copper	10Perc	37	1	3	25	1
	90Perc	66	4	10	51	4
	AV	52	3	6	37	2
Manganese	10Perc	86	0	0	2	0
	90Perc	97	2	1	11	0
	AV	93	1	0	5	0
Nickel	10Perc	68	6	2	8	1
	90Perc	81	13	4	16	2
	AV	75	9	3	12	2
Lead	10Perc	54	2	5	10	1
	90Perc	80	6	14	27	4
	AV	67	4	9	18	2
Antimony	10Perc	38	1	9	2	0
	90Perc	80	5	51	13	4
	AV	61	2	28	7	2
Tin	10Perc	60	2	2	6	0
	90Perc	87	12	9	22	1
	AV	75	6	5	13	0
Vanadium	10Perc	67	10	0	6	1
	90Perc	80	21	1	12	3
	AV	73	15	0	9	2
Zinc	10Perc	22	1	19	11	1
	90Perc	56	4	56	32	2
	AV	39	3	36	21	1

Prim. RM = Primary Raw Materials; Prim. F = Primary Fuels; Sec. F = Secondary Fuels;

Sec. RM = Secondary Raw Materials; Interg. Addit. = Interground Additives

Table 8: **Range of the shares of individual input materials groups in the total trace element concentration of blastfurnace cement, calculated by sensitivity analysis. Values given in percent.**

		share in total content				
		Prim. RM	Prim. F	Sec. F	Sec. RM	Interg. Addit.
Arsenic	10Perc	35	1	0	6	16
	90Perc	72	6	1	13	48
	AV	55	3	1	10	32
Cadmium	10Perc	4	1	1	3	54
	90Perc	25	4	6	15	89
	AV	13	2	3	8	73
Cobalt	10Perc	15	1	1	6	42
	90Perc	43	3	2	14	74
	AV	27	2	1	10	59
Chromium	10Perc	15	0	1	5	56
	90Perc	34	1	2	9	78
	AV	24	1	1	7	67
Copper	10Perc	20	1	2	16	24
	90Perc	47	3	6	32	52
	AV	33	2	4	23	38
Manganese	10Perc	2	0	0	0	82
	90Perc	18	0	0	1	98
	AV	8	0	0	0	91
Nickel	10Perc	37	4	1	6	28
	90Perc	59	8	2	9	48
	AV	48	6	2	7	37
Lead	10Perc	24	1	3	7	26
	90Perc	58	4	8	14	57
	AV	41	2	5	10	42
Antimony	10Perc	9	0	3	1	28
	90Perc	50	2	26	4	81
	AV	28	1	13	2	56
Tin	10Perc	9	1	1	2	43
	90Perc	46	4	3	7	86
	AV	26	2	2	4	66
Vanadium	10Perc	17	3	0	2	52
	90Perc	37	9	0	4	75
	AV	27	6	0	3	64
Zinc	10Perc	9	1	8	5	26
	90Perc	34	2	35	18	67
	AV	21	1	20	11	47

Prim. RM = Primary Raw Materials; Prim. F = Primary Fuels; Sec. F = Secondary Fuels;

Sec. RM = Secondary Raw Materials; Interg. Addit. = Interground Additives

2.4 Range of trace element concentrations in cement: the bottom-up approach

2.4.1 Methodology of the bottom-up approach

The trace element concentrations of German normal cements as measured by the VDZ cover a large range (see table 3, VDZ 10-percentile and 90-percentile values of mixed cement). Among others, this is due to the fact that kinds and quantities of input materials used differ from plant to plant and that trace element concentrations of input materials may vary over a large range.

To reproduce this range of trace element concentrations in cement, further calculations were accomplished for a model plant assuming different scenarios with regard to the composition of input materials (bottom-up approach). These calculations also supply information on the contributions of individual input materials to the total trace element concentration in cement as well as on the range of these contributions.

For the calculations it was assumed that 1.55 t of raw meal are necessary to produce 1 t of clinker and that an energy of 3.6 GJ is needed per ton of clinker.

Regarding the **composition of the raw meals**, various cement standards (lime standard, silicate module, alumina standard) were considered. The modules varied within the usual range and were composed as follows:

Lime standard = $100\ CaO / (2.8\ SiO_2 + 1.8\ Al_2O_3 + 0.65\ Fe_2O_3)$

Silicate module = $SiO_2 / (Al_2O_3 + Fe_2O_3)$

Alumina standard = Al_2O_3 / Fe_2O_3

The **fuels** were assumed to have the following calorific values:

Hard coal	30 MJ/kg
Brown coal	15 MJ/kg
Oil coke	31 MJ/kg
Waste oil	35 MJ/kg
Used tyres	26 MJ/kg
Municipal, commercial and industrial wastes	22 MJ/kg

The composition of the ashes resulting from combustion was not considered when calculating the lime, silicate, and alumina modules. Its effect on the trace element concentrations in cement is assessed to be small.

In the scenarios different compositions of raw meals and fuels were taken into consideration (s. table 9). For all possible combinations of the three raw meals and fuel compositions, the trace element concentrations of cement were calculated. Based on these calculations, the following scenarios were selected for a more detailed analysis:

Scenario A:

Only primary input materials are used. These primary materials are chosen such that the resulting trace element concentrations in cement are as low as possible. Depending on the element, different variants of raw materials and fuels result. For most trace elements the resulting concentration in cement is lowest when the raw meal is composed of limestone and clay stone (raw meal 1) and the fuel consists of brown coal. For manganese, tin, and antimony the fuel consists of hard coal or fuel-mix 1 (s. table A6).

Scenario B:

Since it cannot be assumed that scenario A with a raw meal consisting of limestone and clay stone only and without the addition of iron-containing correction materials, is a realistic one for most of the German cement plants, scenario B was created. In this scenario a raw meal consisting of limestone, clay stone, iron ore, and sand (raw meal 2) was combined with the fuel variant causing the lowest trace element concentration in cement, i.e. use was not limited to primary materials only. As was expected from the trace element concentrations of the input materials given in table A2 in the annex, this fuel variant was identical with that of scenario A.

Scenario C:

This scenario represents the combination of raw meals and fuels, which results in the highest concentration of trace elements in cement, hence, a so-called “worst case” scenario. For all trace elements, this scenario consists of a combination of raw meal 3, consisting of limestone, clay stone, sand, iron ore, *materials from iron and steel industry, and coal fly ash*, and different fuel variants. Combination of raw meal 3 and hard coal leads to high arsenic concentrations in cement. For cobalt raw meal 3 and a fuel mix of 20% used tyres and 80% hard coal (fuel-mix 2) resulted in high trace element concentrations. For cadmium, chromium, copper, manganese, antimony, tin, and zinc raw meal 3 and a fuel mix of 30% municipal, commercial and industrial wastes, 20% used tyres, and 50% hard coal (fuel-mix 3) caused relatively high trace element concentrations in cement (s. table A6). High lead concentrations in cement were obtained when combining raw meal 3 and fuel-mix 4, while high nickel and vanadium concentrations resulted from the use of raw meal 3 and a mix of regular fuels (fuel-mix 1).

Scenario D:

Another scenario that will be described later on serves to determine the extent, to which the mean trace element concentration in cement is caused by the input of secondary fuels and the extent, to which this concentration is reduced when doing without secondary raw materials and interground additives.

The calculations for the scenarios were carried out for **Portland cement and blastfurnace cement**, as these types of cement have turned out to be very different in terms of their trace element concentrations (s. top-down approach, table 3). Moreover, both cements are among the most frequently produced cements in Germany. Both cements were composed according to the European cement standard [DIN EN 197-1] (table 9).

Calculations of the different scenarios were accompanied by studies of the influence of trace element concentration ranges of input materials on the trace element concentrations of cement using sensitivity calculations. The procedure selected has already been described in detail in section 2.3 when presenting the top-down approach. For the evaluations only calculated values in the range of the 10-percentile and 90-percentile values were taken into account.

Table 9: **Composition of raw meal and fuel variants, as well as composition of cements for scenario calculations A, B, and C using the bottom-up approach.**

Raw meal compositions:

	Raw meal 1 %	Raw meal 2 %	Raw meal 3 %
Limestone	80	79.5	79.4
Clay stone	20	18.9	17
Sand	0	0.5	0.5
Iron ore	0	1.1	0.55
Substitutes from iron- and steel works	0	0	0.55
Coal fly ash	0	0	2

	Raw meal 1	Raw meal 2	Raw meal 3	Range*	Average value*
Lime standard	93.5	92.3	93.7	90-104	97
Silicate module	2.6	2.4	2.2	1.6-4.1	2.5
Alumina standard	3.0	2.0	2.0	1.4-3.7	2.3

*Locher, 2000

Fuel compositions: (share referring to applied energy)

Hard coal	100%
Brown coal	100%

Fuel-mix 1	Proportion
Hard coal	50%
Brown coal	35%
Oil coke	15%

Fuel-mix 2	Proportion	Proportion
Used tyres	20%	10%
Hard coal	80%	90%
Used tyres	20%	10%
Brown coal	80%	90%

Fuel-mix 3	Proportion	Proportion	Proportion
Fractions from municipal, industrial and commercial waste	30%	20%	10%
Used tyres	20%	10%	5%
Hard coal	50%	70%	85%
Fractions from municipal, industrial and commercial waste	30%	20%	10%
Used tyres	20%	10%	5%
Brown coal	50%	70%	85%

Fuel-mix 4	Proportion	Proportion	Proportion
Fractions from municipal, industrial and commercial waste	10%	5%	5%
Waste oil	30%	20%	5%
Used tyres	10%	5%	5%
Hard coal	50%	70%	85%
Fractions from municipal, industrial and commercial waste	10%	5%	5%
Waste oil	30%	20%	5%
Used tyres	10%	5%	5%
Brown coal	50%	70%	85%

Sensitivity calculations were performed with values listed in fields highlighted in grey

Composition of cements:

	Portland cement	Blast-furnace cement
Clinker	95%	15%
Coal fly ash	0.2%	
Blast-furnace slag		80%
Gypsum	4.8%	5%

2.4.2 Trace element concentrations of Portland cement and blastfurnace cement and percentage shares of the individual classes of input materials in the total trace element concentrations

The results of the scenario calculations described in the previous section are listed in table A6 in the annex. For each individual trace element and the scenarios described above, the resulting concentration values in Portland cement and blastfurnace cement are shown. Both average values and ranges (10-percentile and 90-percentile values) are indicated. Furthermore, the share of each class of input material in the total concentration is given. For better understanding, figure 26 shows the average trace element concentrations and their ranges in Portland cement for the scenarios A, B, and C.

__Range of trace element concentrations in cement: comparison of scenario and measured values__

The range of trace element contents in cements produced in Germany is supposed to be largely covered by the trace element concentration ranges of Portland and blastfurnace cements as calculated for scenarios A and C. In the following figures, the calculated concentration ranges of selected trace elements (range between the 10-percentile and 90-percentile values) are compared with the analytical values of normal cements as published by the VDZ [VDZ, 2000].

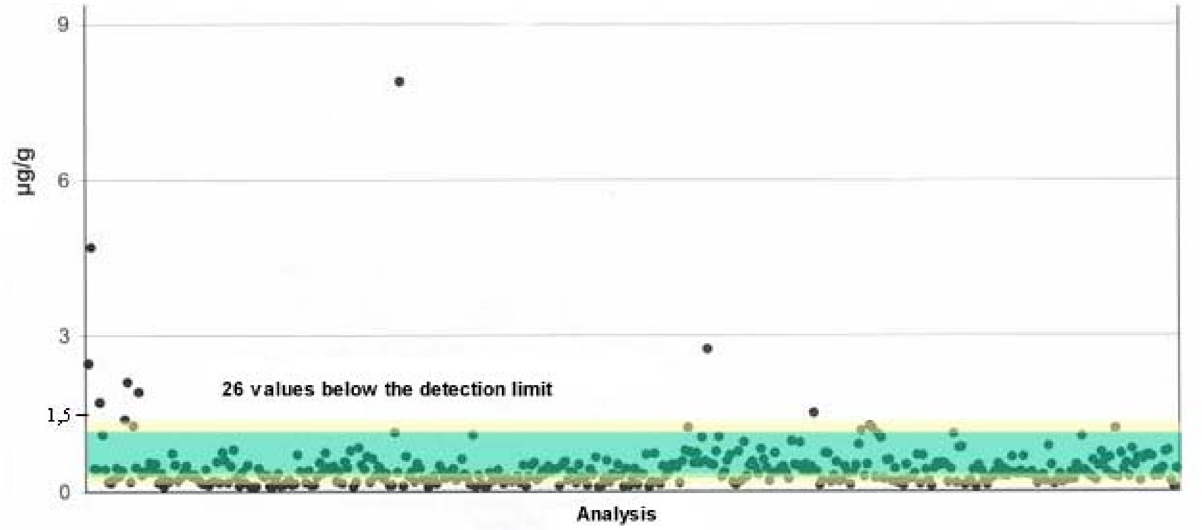


Figure 17: **Measured cadmium contents of normal cements [VDZ, 2000]. Yellow bar: concentration range in Portland cement calculated by the bottom-up approach. Blue bar: concentration range in blastfurnace cement calculated by the bottom-up approach. Green bar: overlapping concentration ranges of Portland and blastfurnace cements.**

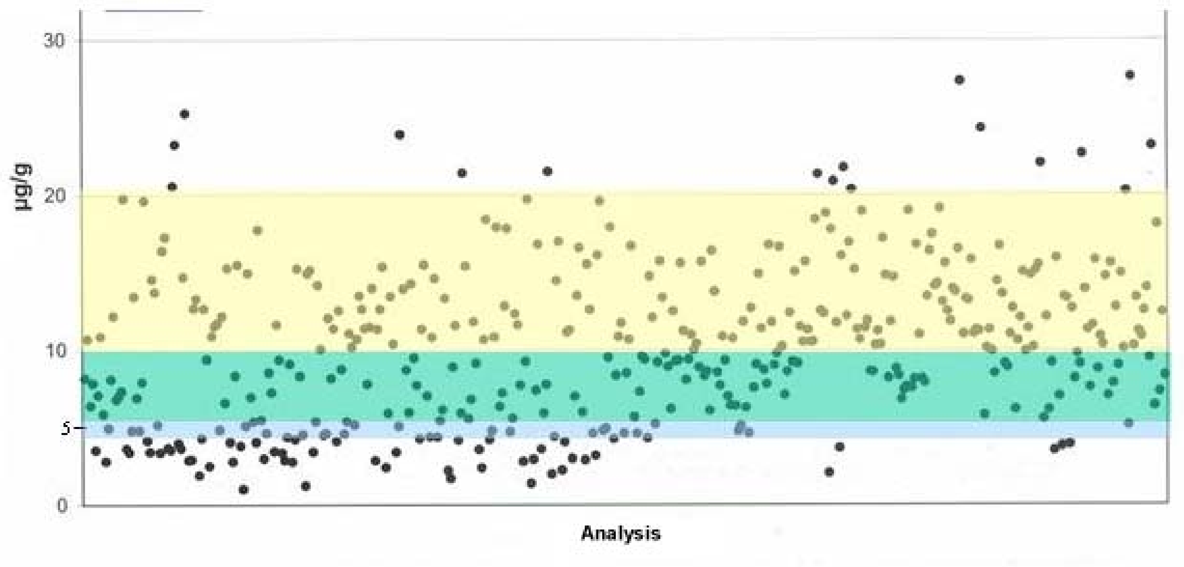


Figure 18: Measured cobalt contents of normal cements [VDZ, 2000]. Yellow bar: concentration range in Portland cement calculated by the bottom-up approach. Blue bar: concentration range in blastfurnace cement calculated by the bottom-up approach. Green bar: overlapping concentration ranges of Portland and blastfurnace cements.

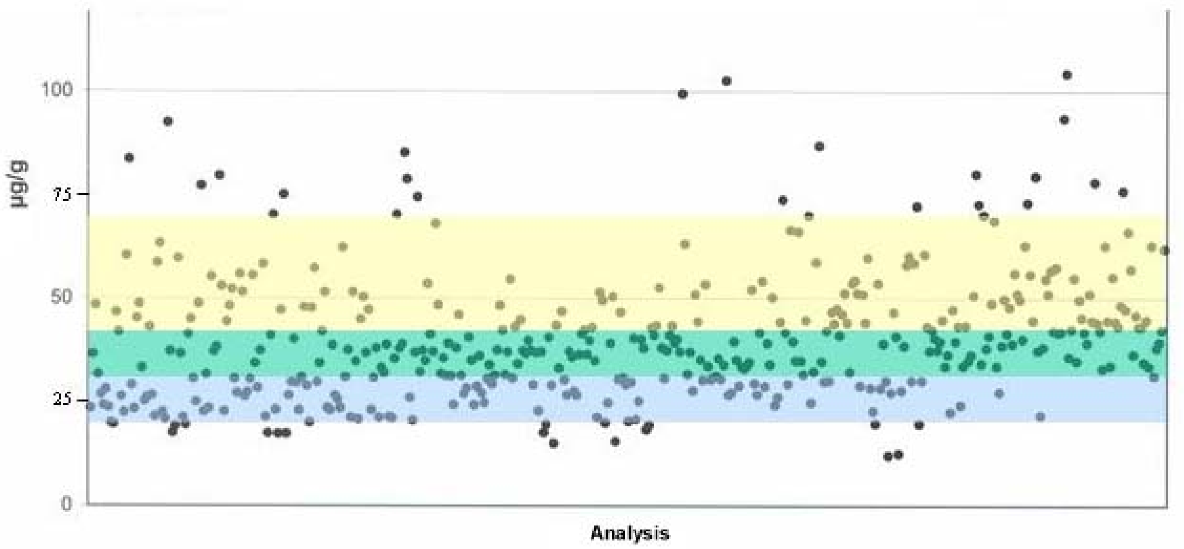


Figure 19: Measured chromium contents of normal cements [VDZ, 2000]. Yellow bar: concentration range in Portland cement calculated by the bottom-up approach. Blue bar: concentration range in blastfurnace cement calculated by the bottom-up approach. Green bar: overlapping concentration ranges of Portland and blastfurnace cements.

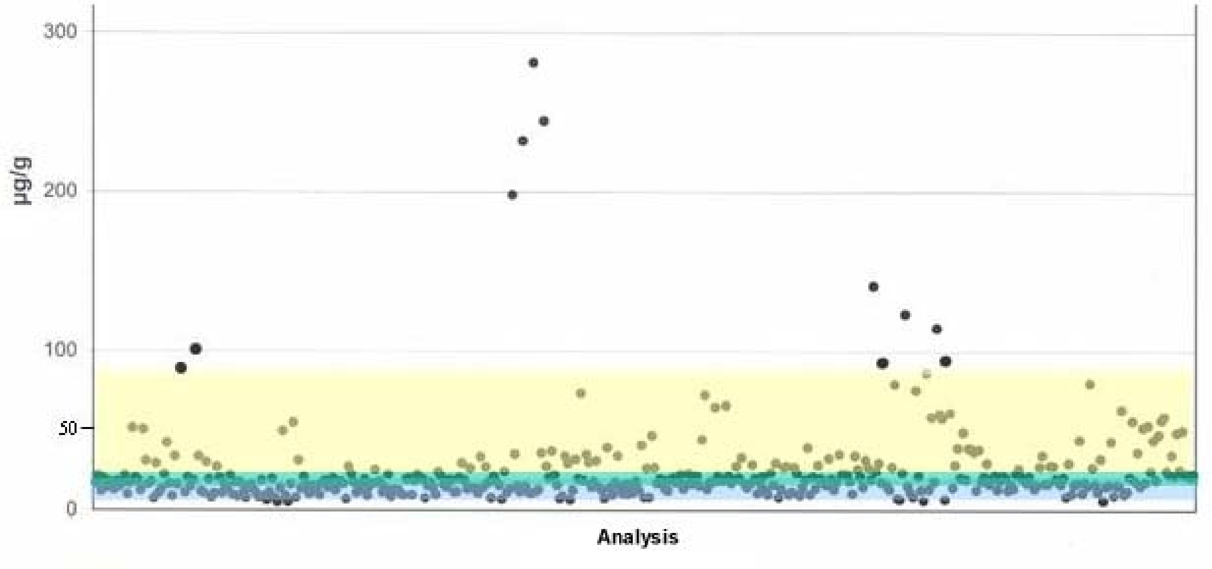


Figure 20: Measured copper contents of normal cements [VDZ, 2000]. Yellow bar: concentration range in Portland cement calculated by the bottom-up approach. Blue bar: concentration range in blastfurnace cement calculated by the bottom-up approach. Green bar: overlapping concentration ranges of Portland and blastfurnace cements.

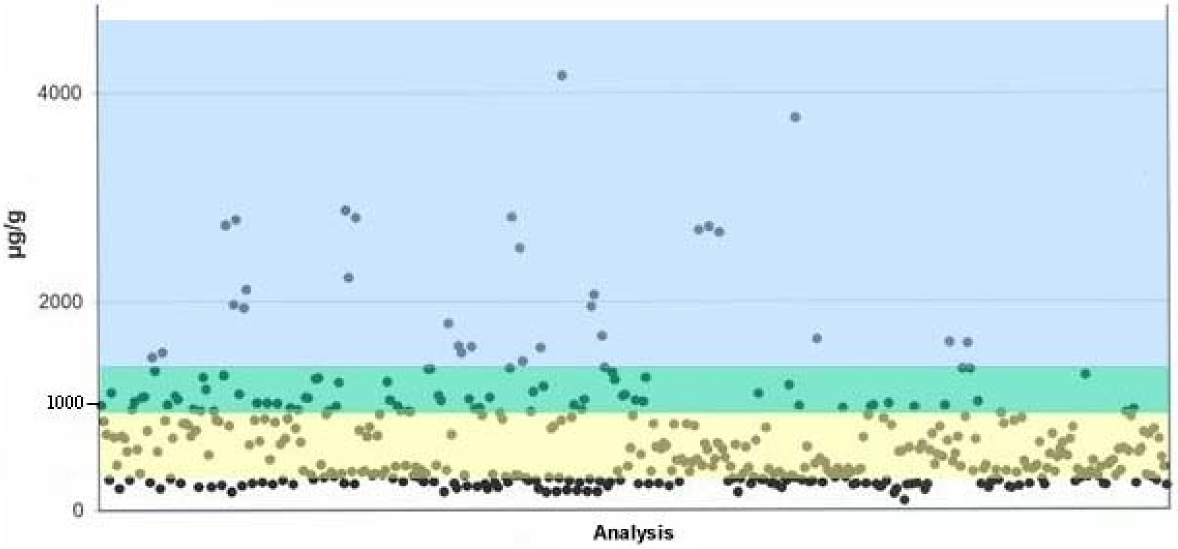


Figure 21: Measured manganese contents of normal cements [VDZ, 2000]. Yellow bar: concentration range in Portland cement calculated by the bottom-up approach. Blue bar: concentration range in blastfurnace cement calculated by the bottom-up approach. Green bar: overlapping concentration ranges of Portland and blastfurnace cements.

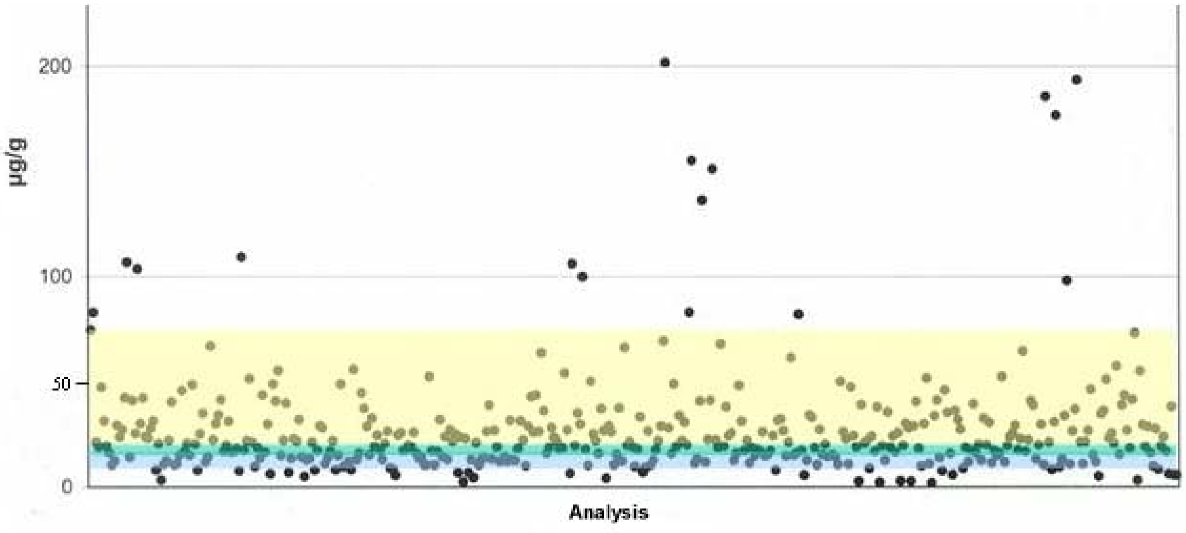


Figure 22: Measured lead contents of normal cements [VDZ, 2000]. Yellow bar: concentration range in Portland cement calculated by the bottom-up approach. Blue bar: concentration range in blastfurnace cement calculated by the bottom-up approach. Green bar: overlapping concentration ranges of Portland and blastfurnace cements.

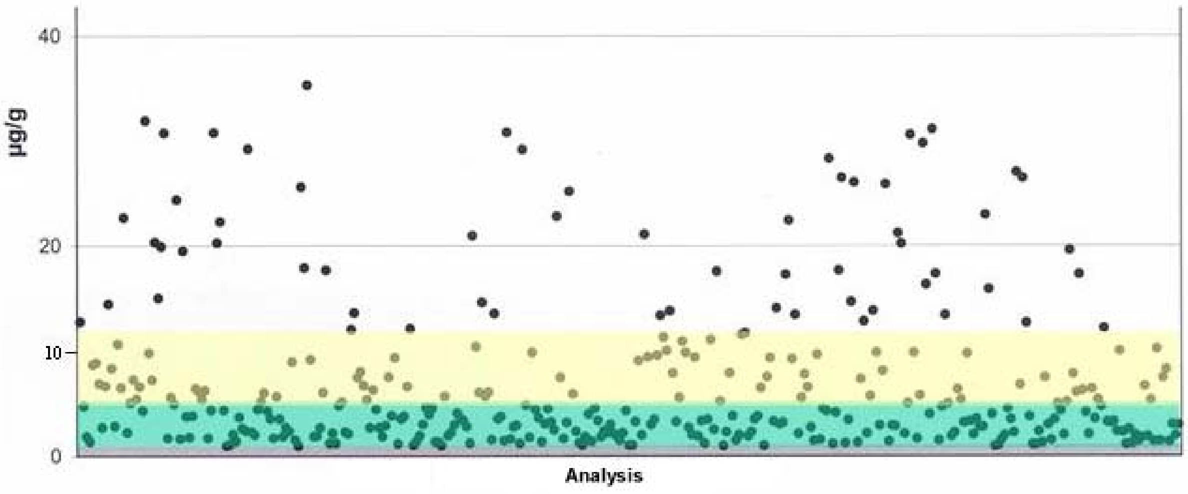


Figure 23: Measured antimony contents of normal cements [VDZ, 2000]. Yellow bar: concentration range in Portland cement calculated by the bottom-up approach. Blue bar: concentration range in blastfurnace cement calculated by the bottom-up approach. Green bar: overlapping concentration ranges of Portland and blastfurnace cements.

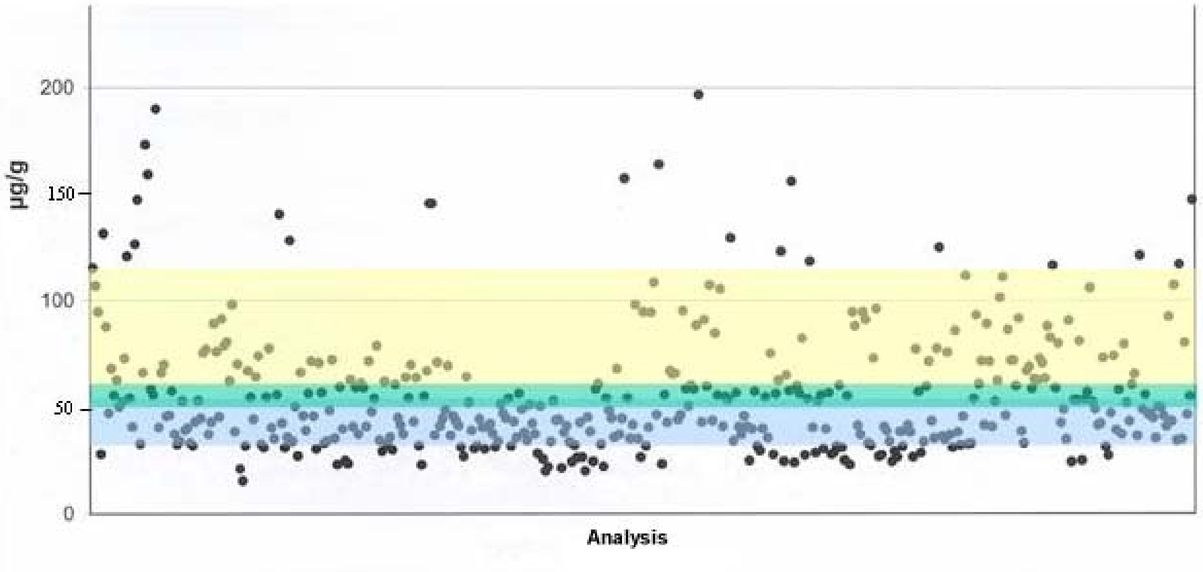


Figure 24: **Measured vanadium contents of normal cements [VDZ, 2000]. Yellow bar: concentration range in Portland cement calculated by the bottom-up approach. Blue bar: concentration range in blastfurnace cement calculated by the bottom-up approach. Green bar: overlapping concentration ranges of Portland and blastfurnace cements.**

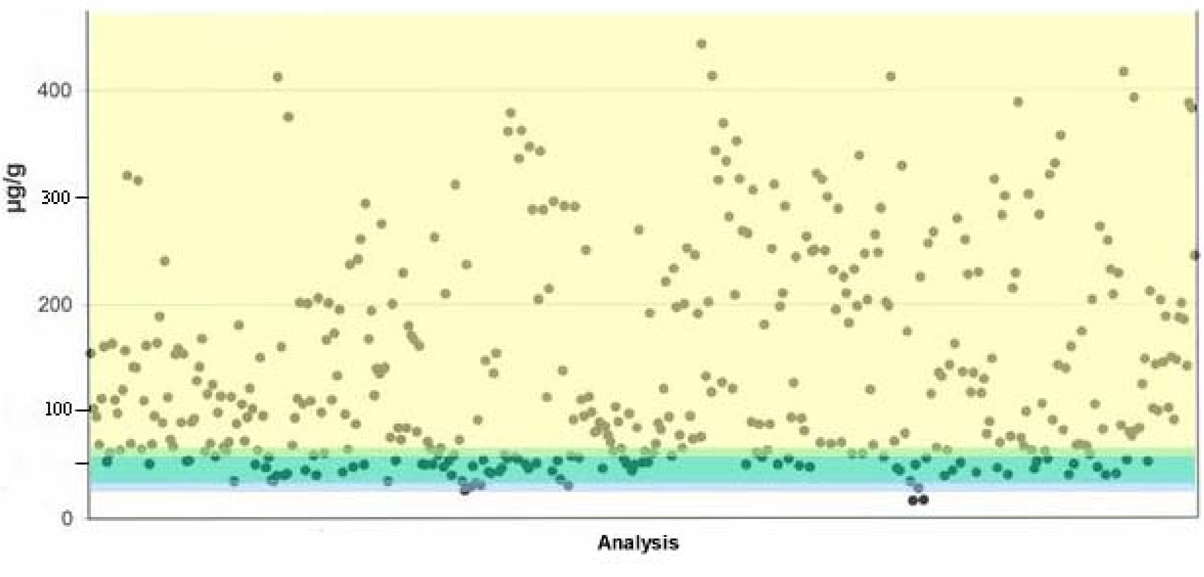


Figure 25: **Measured zinc contents of normal cements [VDZ, 2000]. Yellow bar: concentration range in Portland cement calculated by the bottom-up approach. Blue bar: concentration range in blastfurnace cement calculated by the bottom-up approach. Green bar: overlapping concentration ranges of Portland and blastfurnace cements.**

As obvious from the figures, the range of values measured for the trace elements cadmium, cobalt, chromium, copper, lead, vanadium, and zinc is covered well by the scenarios. However, this is not the case for manganese and antimony. The manganese concentration range calculated is higher than that of the measured values. Most of the measurement points of antimony are not covered by the scenarios (s. figure 23). A reason why many values measured exceed the values calculated may be found in plastic waste that sometimes may contain high concentrations of antimony. The current BUWAL debate on revised guide values for pollutant loads of waste and the modification of the environmental tolerance value for antimony illustrates that plastics represent a major input path of antimony into cement [BUWAL Revisionskommission, Nov. 2001]. Antimony compounds are applied in PET production. For further use of plastics as input materials in cement production, the guide value in the positive list for antimony in plastics was increased from 5 to 300 ppm [BUWAL Positivliste, 2001]. Also in Germany, this problem is being discussed. The Federal Association on the Quality of Secondary Fuels currently considers an increase in the guide value for antimony in secondary fuels from municipal waste, which presently amounts to 25 ppm (median). To cover the upper range of antimony concentrations measured by the VDZ, bottom-up calculation would have to use the actual mean values of antimony in iron and steel wastes instead of the mean minimum values applied so far (s. table A2). Moreover, antimony concentration of municipal, commercial and industrial wastes would have to be assumed to be increased by several factors. In contrast to this, doubling or triplication of antimony contents of the raw meal does not affect the concentration values calculated, as these concentrations are far smaller than those of the waste.

Influence of waste utilisation on the trace element contents of cement

It is the purpose of the bottom-up approach to estimate the potential lower and upper limits of the trace element concentrations of cement through scenarios, on the one hand, and to find out how the trace element concentration of cement or its range changes, if certain wastes are applied. The concentration ranges of trace elements in cement were dealt with in the previous section. The sections below now focus on the possible influence of waste utilisation on the trace element concentration of cement.

The possible influence of waste utilisation on trace element concentrations in cement can be seen by comparing the ranges of the trace element concentrations in the three scenarios A, B, and C. Based on the data given in table A6, the trace element concentration ranges of various cements are represented as average, 10-percentile and 90-percentile values in figure 26.

It is focussed on the comparison of scenario B (raw meal 2 containing iron ore, but no other secondary raw materials, combined with fossil fuels) and scenario C (raw meal 3 containing secondary raw materials combined with mixtures of secondary fuels), i.e. cements with and without the use of waste as input material are compared. If the trace element concentration ranges resulting from the two scenarios do not overlap, it may be assumed that the use of waste has an influence on the trace element concentration of cement. This was confirmed for cadmium, antimony, and zinc. The trace element concentration ranges obtained for these three elements in both scenarios do not overlap. If no wastes were used, concentration of these trace elements in cement could be reduced significantly within the scenarios observed.

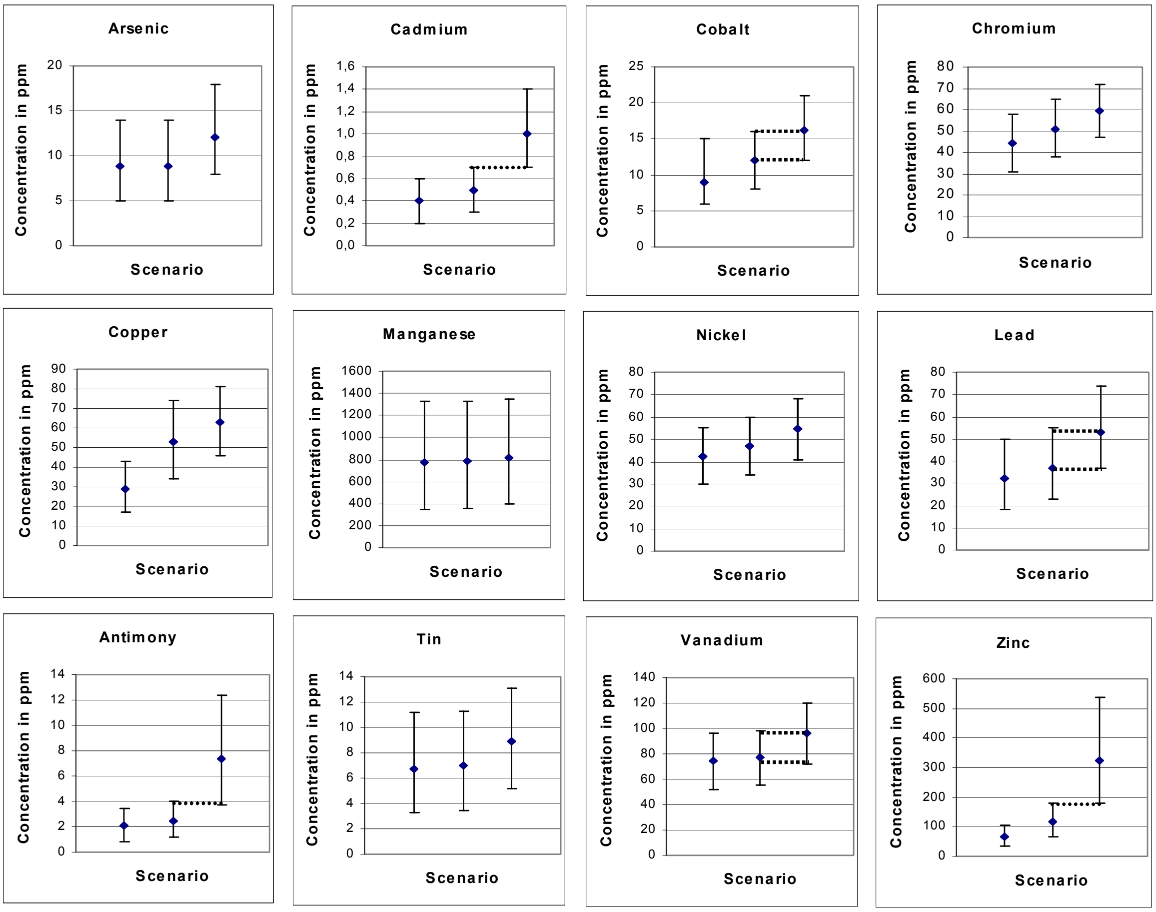


Figure 26: **Average trace element concentrations and their ranges in Portland cement in scenarios A (left), B (middle), and C (right).**

For cobalt, lead, and vanadium the ranges overlap. However, the average values of scenario C lie at the edge or outside of the range of scenario B. This means that an influence of the use of waste as input material on trace element concentrations in cement can be noticed, although it is not as distinct as for cadmium, antimony, and zinc. For all other trace elements the ranges of concentrations in cement overlap for scenarios B and C. Only the average values differ. Consequently, the effect of the use of wastes on trace element concentrations in cement cannot be demonstrated clearly.

When comparing scenarios B and C, it must be kept in mind that the trace element concentrations of the substitute materials from iron and steel industry used for the calculations do not represent average values as for all other input materials, but average minimum values (s. table A2 in the annex). If calculations would have been performed with the average values, discrepancy of the three scenarios would have been even larger.

The importance of secondary raw materials and fuels as well as of interground additives as input paths of trace elements into cement for scenario C

To calculate the trace element contents of Portland cement for the different scenarios, a certain raw meal was combined with certain fuels and interground additives. Now, it shall be studied, which input paths are responsible for the high trace element concentrations calculated in the “worst case” scenario C. Particular attention is paid to trace elements that are input largely via secondary materials, such as cadmium, cobalt, chromium, copper, lead, antimony, tin, and zinc (s. table A6 in the annex). Secondary fuels are of current political interest, as they are suspected to represent a major input path for individual trace elements. While for antimony and zinc secondary fuels clearly represent the most important input path (60 and 56%), secondary raw materials also represent an important source of cadmium, cobalt, chromium, copper, and lead and must not be neglected as input path.

Scenario D: production of cement without the addition of secondary raw materials and interground additives

Scenario D serves to investigate the extent, to which the mean trace element concentration in cement is caused by the input of secondary fuels and the reduction of the trace element concentration when doing without secondary raw materials and interground additives. Raw meal 2 (limestone, clay stone, sand, and iron ore) was combined with a fuel mix causing the highest trace element concentrations in Portland cement. The Portland cement studied only consisted of clinker and gypsum, coal fly ash was not applied (s. table 10). As compared to the “worst case” scenario C, the cement did not contain any substitute materials from iron and steel industry or coal fly ash, while the remaining input materials were the same. For arsenic, nickel, and vanadium this scenario calculation was not carried out, as the maximum contents of these trace elements are reached by the use of regular fuels. Secondary fuels are of minor importance to these trace elements.

Table 10: **Composition of the raw meal and fuel variants as well as of the Portland cement for scenario calculation D using the bottom-up approach.**

Raw meal composition:

	Raw meal %
Limestone	79.5
Clay stone	18.9
Sand	0.5
Iron ore	1.1
Substitutes from iron- and steel works	0
Coal fly ash	0

Fuel compositions: (share referring to applied energy)

Fuel-mix 2	Proportion
Used tyres	20%
Hard coal	80%

Fuel-mix 3	Proportion
Fractions from municipal, industrial and commercial waste	30%
Used tyres	20%
Hard coal	50%

Fuel-mix 4	Proportion
Fractions from municipal, industrial and commercial waste	10%
Waste oil	30%
Used tyres	10%
Hard coal	50%

Composition of cement:

Clinker	95%
Coal fly ash	
Blast-furnace slag	
Gypsum	5%

As illustrated by table A7 (annex), no significant reduction of the trace element concentration ranges in cement was reached with scenario D. Trace element concentrations of scenarios C and D lie in a similar range. Only for the elements cadmium, cobalt, and lead are the concentration values in scenario D reduced by 20, 13, and 19%, respectively, as compared to scenario C.

Cadmium concentration in cement is reduced when doing without substitute materials from iron and steel industry. This is indicated by the high cadmium concentrations of these substitute materials (see average minimum contents in table A2 in the annex). For cobalt, however, the situation is different. Cobalt concentration in cement can be reduced by doing without the use of coal fly ashes, as cobalt reaches relatively high concentrations in coal fly ash as compared to other input materials. As far as cobalt is concerned, the doing without substitute materials from iron and steel industry hardly has any effect, since cobalt concentrations in the substitute materials from iron and steel industry and iron ore are relatively similar (s. table A2 in the annex). Lead assumes an intermediate position. In coal fly ashes it reaches a relatively high concentration. Lead concentrations in the substitute materials from iron and steel industry exceed those of iron ore.

Regarding chromium and copper, secondary raw materials represent a major input path (s. table A6, annex). Nevertheless, the doing without secondary raw materials and interground additives in scenario D hardly has any impact on chromium and copper concentrations in cement (s. table A7, annex). This is due to the fact that concentrations of these trace elements in iron ore are similar to or even higher than those of the substitute materials from iron and steel industry, while concentrations in coal fly ashes are small. Iron ore is a correction material, but not classified as waste material and, hence, takes a special position in the calculations. When estimating the input paths in the top-down and bottom-up approach, iron ore was assigned to the group of secondary raw materials. In scenario D, however, in which no secondary raw materials or interground additives were used, the raw meal contained iron ore. If no iron ore was used in the raw meal under scenario D, the average chromium and copper concentrations would have been reduced significantly in cement.

The slight reduction of the average concentrations of antimony and zinc in scenario D as compared to scenario C underlines the importance of secondary fuels as input path.

2.5 Own Cement Analyses

The analytical data published in literature with regard to the trace element concentration of cement are several years old ([VDZ, 2000]: Sampling 1998). To illustrate the current situation in Germany, 8 CEM I, 8 CEM II, 1 CEM III, and, for comparison, a non-standardised aluminous cement were procured in 2002 and analysed twice for arsenic, beryllium, lead, chromium, cobalt, copper, manganese, nickel, and zinc using ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy). The results of both measurements were averaged.

For decomposition water, HNO_3, HF, and HCl were added to the samples (about 100 mg). Then, the samples were subjected to microwave treatment at 220°C for 40 minutes. Upon the addition of H_3BO_3, the solutions were heated in a microwave at 160°C for six minutes again.

The ICP-OES was calibrated with a soil standard. Prior to the measurements, two blank samples each were analysed. The average blank value was then deducted from the measured sample concentrations. The measurement results and the detection limits reached are presented in table 11.

Compared to the average values published by the VDZ for 1998, the 2002 average arsenic and zinc contents of normal cement are much higher. For both elements as well as for beryllium and manganese the peak values given by the VDZ also were exceeded considerably. However, the small number of samples does not allow to postulate a general increase in trace element contents within the past three years. Non-standardised aluminous cement was analysed for comparison only. It is mainly used as e.g. wash floor when completing the interior. Compared to normal cements, concentrations of some low-volatile trace elements (Be, Co, Cr, and Ni) are increased significantly.

Table 11: Trace element concentrations of normal cements 1998 [VDZ, 2000] and of normal cements and aluminous cement 2002 (own analyses). The data collected by the VDZ in 1998 comprise more than 410 samples. Own analyses covered 18 cements procured on the market (8 CEM I samples, 8 CEM II samples, 1 sample of CEM III, and, for comparison, a non-standardised aluminous cement = AC). AV = Average values; DL = Detection limit.

	Normal cements 1998, n ≈ 410 [ppm] [VDZ, 2000]		Forschungszentrum Karlsruhe (2002) [ppm]						
			CEM I n=8		CEM II n=8		CEM III n=1	AC n=1	DL
	max.	AV	max.	AV	max.	AV		Non standardised	
As	55	6.8	**110**	33	51	14	8	40	9
Be	2.5	0.7	1.6	0.9	2.0	1.1	**2.9**	**4.0**	0.1
Co	28	10	11	7	11	8	7	**32**	1
Cr	110	40	60	31	98	48	59	**696**	1
Cu	280	25	41	21	23	20	15	11	1
Mn	4200	680	1654	805	1037	565	**7385**	364	0.1
Ni	80	24	41	20	39	20	14	**203**	8
Pb	200	27	106	41	37	23	13	53	6
Zn	440	140	**657**	282	**673**	237	302	36	0.4

	Van der Sloot et al., (2001) [ppm]		Forschungszentrum Karlsruhe 2002 [ppm]						
			CEM I n=8		CEM II n=8		CEM III n=1	AC n=1	NWG
	max.	AV	max.	AV	max.	AV		Non standardised	
Mo	-	1-8	3.8	2.0	5.0	1.9	1.4	9.5	1.1

Average values: contents below the detection limit were considered with a value equivalent to half of the detection limit (VDZ and own analyses). Bold: Maximum value exceeds the maximum content measured by VDZ (2000). Grey: Average value is more than twice as high as the average value measured by VDZ (2000).

2.6 Estimation of trace element transfer into concrete

2.6.1 Methodological approach

In the preceding sections, trace element concentrations of cement were calculated, the calculated values were compared with measurements, and the relevance of the individual input paths was studied. In building industry, cement only is an intermediate product used for the production of concrete. From the ecological point of view, concrete therefore also is of interest. For this reason, the input paths of trace elements into concrete shall now be investigated in more detail.

To estimate the trace element transfer into concrete, four concretes were modelled and compared with each other. The concretes consisted of two different cements, water, two different mixtures of aggregates, and coal fly ash. For comparison, the types of cement most frequently produced in Germany, namely, Portland cement and blastfurnace cement, were used, which strongly differ in their trace element concentrations. Two extreme cases of aggregates were selected. A mixture of gravel (coarse aggregate) and sand (fine aggregate) with a relatively small trace element concentration was compared with a mixture of basalt (coarse aggregate) having relatively high trace element concentrations and a hypothetical slag (fine aggregate), i.e. a mixture of slag from iron and metal works with one third of fine grains. Hereinafter, the latter shall be referred to as slag.

The concrete recipes were composed in accordance with the following equation:

$$z/Q_z + w/Q_w + g/Q_g + zs/Q_{zs} + \text{pores} = 1000 \qquad [1]$$

where

z = mass of cement (kg/m^3)

w = water mass (kg/m^3)

g = mass of aggregate (kg/m^3)

zs = mass of coal fly ash (kg/m^3)

Q = density of the respective material (kg/dm^3)

pores = air pore volume

The assumption was based on 350 kg of cement per cubic meter of concrete, a water-to-cement ratio (w/z value) of 0.45, 2% (mass) of coal fly ashes, 1% pores, and a grading curve 3 (according to DIN EN 1045-2 for an aggregate mixture of 0-32 mm). The ratio of coarse to fine aggregates was 53 to 47. When composing the concretes, water consumption of the coal fly ash was taken into account. The four concrete variants are composed as follows (table 12):

Table 12: **Composition of concrete variants composed of different types of cement and aggregates as well as of water and coal fly ash. Slag*: hypothetical slag, consisting of slags from iron and metal works.**

	Concrete 1	Concrete 2	Concrete 3	Concrete 4
Sand/Gravel aggregates	77%	77%		
Basalt/Slag* aggregates			78%	78%
Portland cement		14%		14%
Blastfurnace cement	14%		14%	
Water	7%	7%	6%	6%
Coal fly ash	2%	2%	2%	2%

Combination of both aggregates with the two cements, i.e. Portland cement and blastfurnace cement, yielded four variants of concrete in total.

The average trace element concentrations of the concrete input materials of water, aggregates, and coal fly ash were taken from literature. Regarding the trace element contents of water, the Drinking Water Regulations were applied, and it was assumed that the mean concentrations corresponded to the limit values given in the Drinking Water Regulations of 2001, annex 2, parts I and II. The trace element concentrations of the input materials used for the calculation are given in table A8 in the annex. To make a statement with regard to the trace element concentration ranges in concrete, sensitivity calculations were performed, as described in section 2.3.3, taking into account the distribution of the trace element concentrations in the input materials of water, coal fly ash, and aggregates. Trace element concentrations of

Portland cement and blastfurnace cement were taken from the sensitivity calculations made within the framework of the top-down approach (see section 2.3).

As no reliable data exist for the antimony concentration in sand, gravel, basalt, and slag, no calculations could be performed to determine the antimony concentration in concrete.

2.6.2 Trace element concentrations of concrete

Concrete from Portland cement

Figure 27 shows evaluations for concrete with Portland cement as bonding agent. For the individual elements values for raw meal, clinker, Portland cement, concrete from Portland cement with basalt and slag aggregates as well as for concrete from Portland cement with sand and gravel aggregates are given, normalised to the trace element concentration in raw meal. Values above 1 mean an increase of concentration as compared to raw meal. The mean trace element concentrations of raw meal, clinker, and cement were taken from table 3, the mean trace element concentrations of concrete were taken from table A10 (annex).

In any case, the increase in concentrations from raw meal to clinker, as discussed in the previous sections, is clearly noticeable. This increase is attributed among others to the escape of CO_2 (for 1 t clinker 1.55 t of raw meal are needed). A far higher increase is noticed for cadmium and zinc. Clinker and Portland cement exhibit slight element concentration differences only, as Portland cement consists of 99% of clinker.

In the concrete produced with the basalt-slag aggregate concentrations of arsenic, lead, tin, and zinc decrease or lie in the same range as in cement. For cadmium and nickel concentrations increase slightly. For cobalt, chromium, copper, manganese, and vanadium significant increases are observed.

In concrete containing a sand/gravel aggregate most element concentrations are found to be far smaller than in cement. For manganese, nickel, lead, tin, vanadium, and zinc values even are in the range of or below the values of raw meal.

As a whole, four categories can be distinguished as far as the distribution of trace elements to raw meal, clinker/Portland cement, concrete (basalt/slag), and concrete (gravel/sand) is concerned (s. table 13). Vanadium may be assigned to both categories I and II, as its concentrations in raw meal and concrete (gravel/sand) are almost the same.

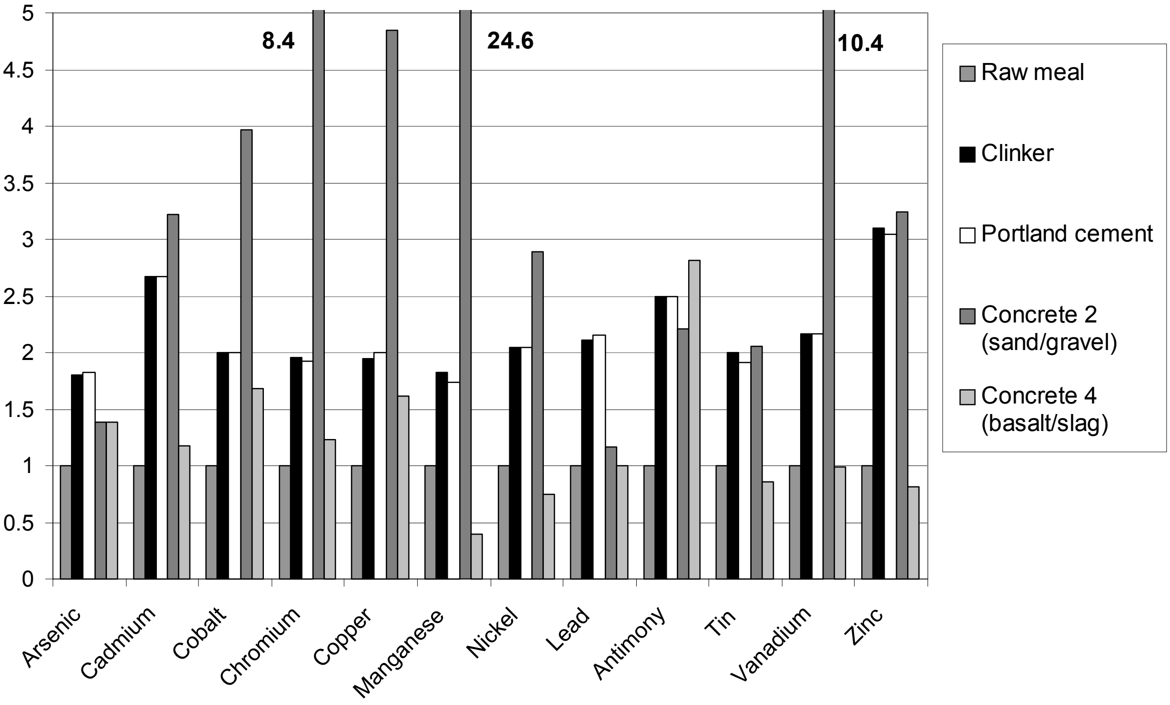


Figure 27: **Comparison of the trace element concentrations in concretes from Portland cement with those of raw meal, clinker, and Portland cement. Normalisation to raw meal.**

To sum up, it may be stated that in categories I and II the trace element content of concrete (B/Sl) increases as compared to that of cement. For the other categories trace element concentrations in cement are either higher or of the same order of magnitude as in concrete (B/Sl).

Table 13: **Order of distribution of trace elements to raw meal, clinker/Portland cement, concrete (basalt/slag*), and concrete (gravel/sand), and distinction of four categories according to the relevance criterion. Slag*: hypothetical mixture of slags from iron and metal works.**

	Order of relevance	Trace element
I	Concrete (B/Sl) > Clinker/Cement > Concrete (G/S) > Raw meal	Cd, Co, Cr, Cu, V
II	Concrete (B/Sl) > Clinker/Cement > Raw meal > Concrete (G/S)	Mn, Ni, V
III	Concrete (B/Sl) = Clinker/Cement > Raw meal > Concrete (G/S)	Sn, Zn
IV	Clinker/Cement > Concrete (B/Sl) >/= Concrete (G/S) = Raw meal	As, Pb

Concrete (B/Sl) = Concrete from Basalt / Slag*; Concrete (G/S) = Concrete from Gravel / Sand

Concrete from blastfurnace cement

For concrete from blastfurnace cement, the same conclusions can be drawn from the comparison of raw meal with clinker as for Portland cement, as the same input materials are applied.

As obvious from figure 28, concentration of all elements – except for manganese – is far smaller in cement than in clinker. For the elements arsenic, copper, nickel, and lead, values are even found to be below the values for raw meal. This can be explained by the low trace element concentrations of granulated blast-furnace slag as well as by the high proportion of granulated blast-furnace slag in cement.

In concrete produced with a basalt/slag aggregate arsenic, lead, tin, and zinc concentrations decrease in comparison with clinker or are found to be in the similar range. Compared to clinker, cadmium and nickel concentrations are found to be slightly increased. For cobalt, chromium, copper, manganese, and vanadium significant increases are observed. These results are in agreement with the results obtained for concrete from Portland cement.

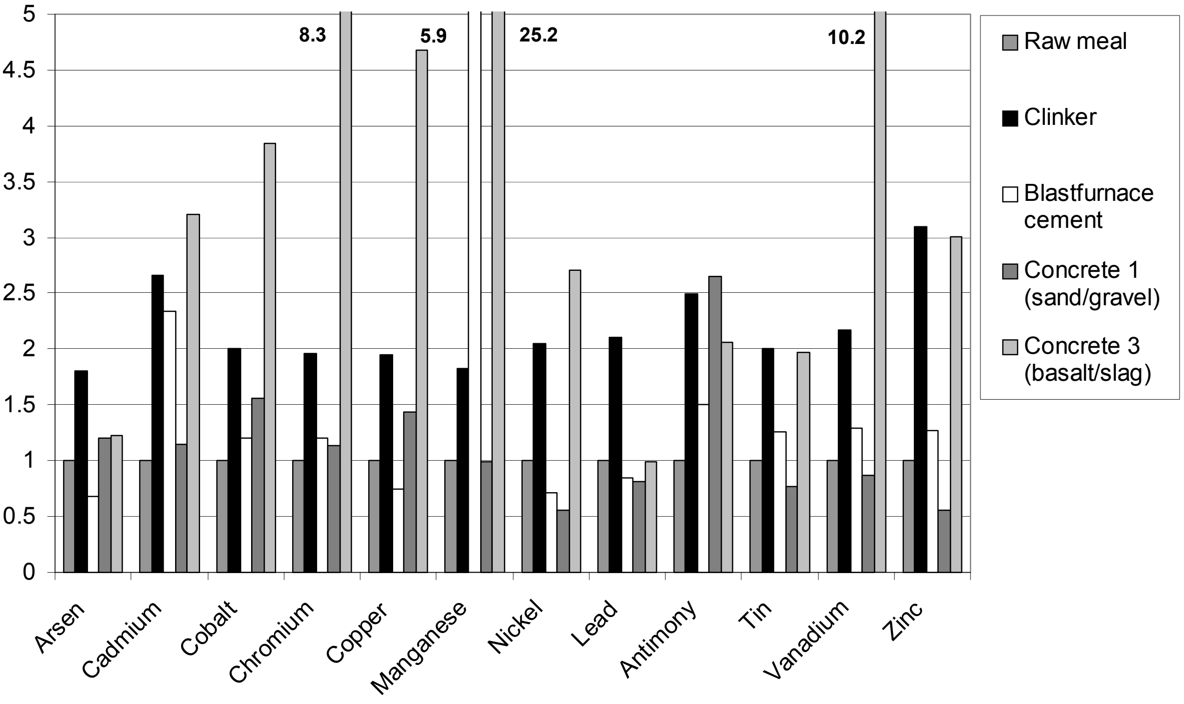


Figure 28: **Comparison of the trace element concentrations in concretes from blastfurnace cement with those of raw meal, clinker, and blastfurnace cement. Normalisation to raw meal.**

Concentrations of cadmium, manganese, nickel, tin, vanadium, and zinc in concrete with sand/gravel aggregates are lower than in cement. Partly, the values are found to be even below those of raw meal. For most of the remaining elements the concentrations are found to lie in the range of the values of cement. Only for arsenic, cobalt, and copper does a moderate increase occur as compared to the concentrations in cement.

In concrete with basalt/slag aggregates concentrations of all elements are higher than in concrete with sand/gravel aggregates.

When comparing concrete having a Portland cement bonding agent with concrete having a blastfurnace cement bonding agent, concentrations of all elements differ slightly only.

This is also visible from table A10 in the annex. Table A10 shows the results of the calculations made for the four concrete variants, including the results of sensitivity analysis. Apart from the average trace element concentration and the concentration range (10-percentile to 90-percentile) in the concretes, the shares of the individual input materials (in percent) in the total content are represented. To illustrate the information given in the table, the results obtained for selected trace elements are represented in the figures below. One or two representatives each have been selected from the categories I, II, and IV given in table 13. In addition to average concentration values of these trace elements, the range of the values (10-percentile to 90-percentile values) and the shares of the individual input materials in the total trace element concentration of concrete are shown in figures 29 through 32.

The colours of the table and the figures are chosen such that fractions which are potentially mobilisable in the long term are coloured red, while fractions which are rather immobile in the long term are coloured green. This classification is based on a rough estimation of the mobility behaviour under physical aspects. Accordingly, trace elements in media with a large surface to volume ratio (potentially higher dissolution kinetics) may be classified as potentially mobilisable. The bonding agents cement and coal fly ash belong to this group of materials. Green colours have been selected for dense media, e.g. concrete aggregates, which have a small specific surface area, which is why trace elements are contained in a rather immobile form. Slags from iron and metal works with a high proportion of fine grain take a special position. Slags from high-temperature processes have a dense, glazed consistency. Due to the larger surface area, the fine grain fraction is supposed to have an increased reactivity.

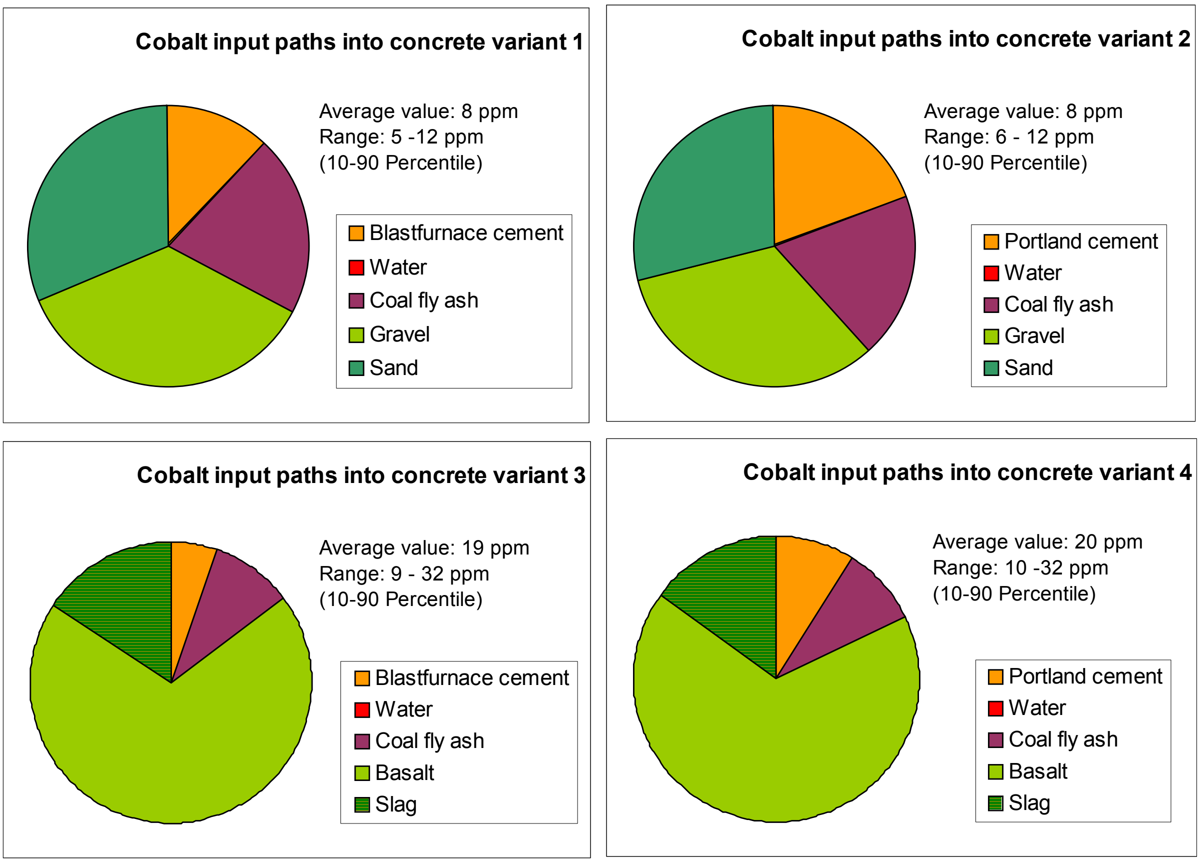


Figure 29: **Mean cobalt concentrations and concentration ranges in the four concrete variants. Relative shares of the individual input materials in the total cobalt concentration of concrete.**

For a detailed analysis and evaluation of the mobility behaviour, however, also the chemical mobility of the trace elements integrated in the individual concrete components must be taken into consideration. This topic shall be dealt with in more detail in section 3.1.

Cobalt and chromium are representatives of category I (table 13). Concentration of both is higher in concrete (basalt/slag) than in clinker (figure 28). Comparison of the elements cobalt and chromium (figures 29 and 30) reveals that the distribution of the trace element input to the individual input paths is similar for concretes from sand/gravel. For concretes from basalt and slag cobalt distribution completely differs from that of chromium. For both elements, however, aggregates represent a major input source. While cobalt is largely input from basalt, input from the slag predominates for chromium. About 17% of cobalt input occurs from coal fly ash and cement. For chromium the input via these materials plays a minor role. Again, it must be noted that the mean chromium concentrations in concretes from basalt and slag by far exceed those of concretes from sand/gravel (s. figures 27 and 28).

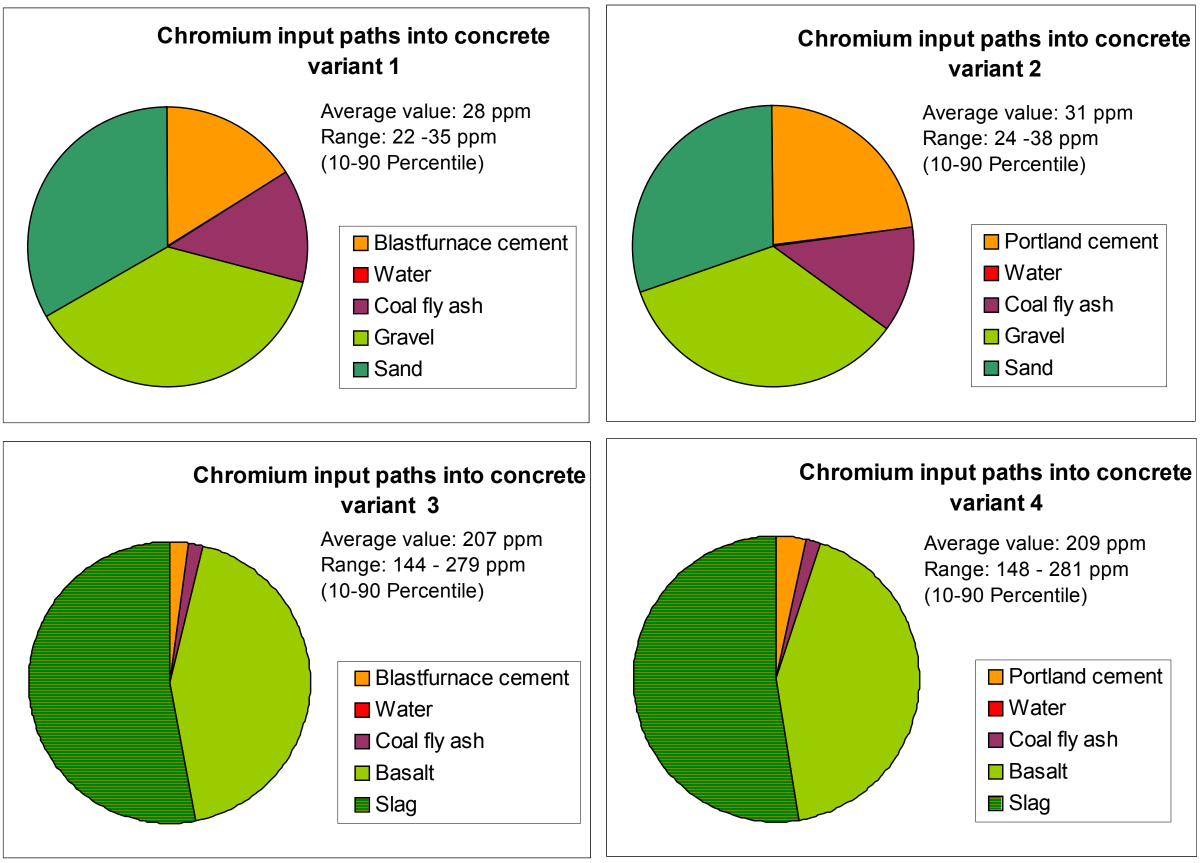


Figure 30: **Mean chromium concentrations and concentration ranges in the four concrete variants. Relative shares of the individual input materials in the total chromium concentration of concrete.**

Nickel concentration in concrete (basalt/slag) also exceeds that of clinker. However, lowest concentrations are encountered in concrete from gravel/sand.

Figure 31 shows the nickel input paths into concrete (basalt/slag), the distribution being similar to that of cobalt. Coal fly ash and cement, however, reach higher shares for the input into concrete from gravel/sand. This is mainly due to the much smaller nickel contents of sand/gravel as compared to coal fly ashes or sand (s. tables 3 and A8 in the annex). The high nickel concentrations of concrete from basalt/slag are mainly attributed to the input from basalt.

An input distribution similar to that of nickel into concrete from gravel/sand is exhibited by lead, a representative of the fourth category. Also the lead input mainly occurs by coal fly ashes and cement. Figure 32 shows that red colours predominate for all four types of concrete, reflecting the predominance of materials that contain potentially mobilisable trace elements. It has to be taken into account, however, that lead contents in all types of concrete are only half as high as the lead contents of Portland cement (s. figure 27).

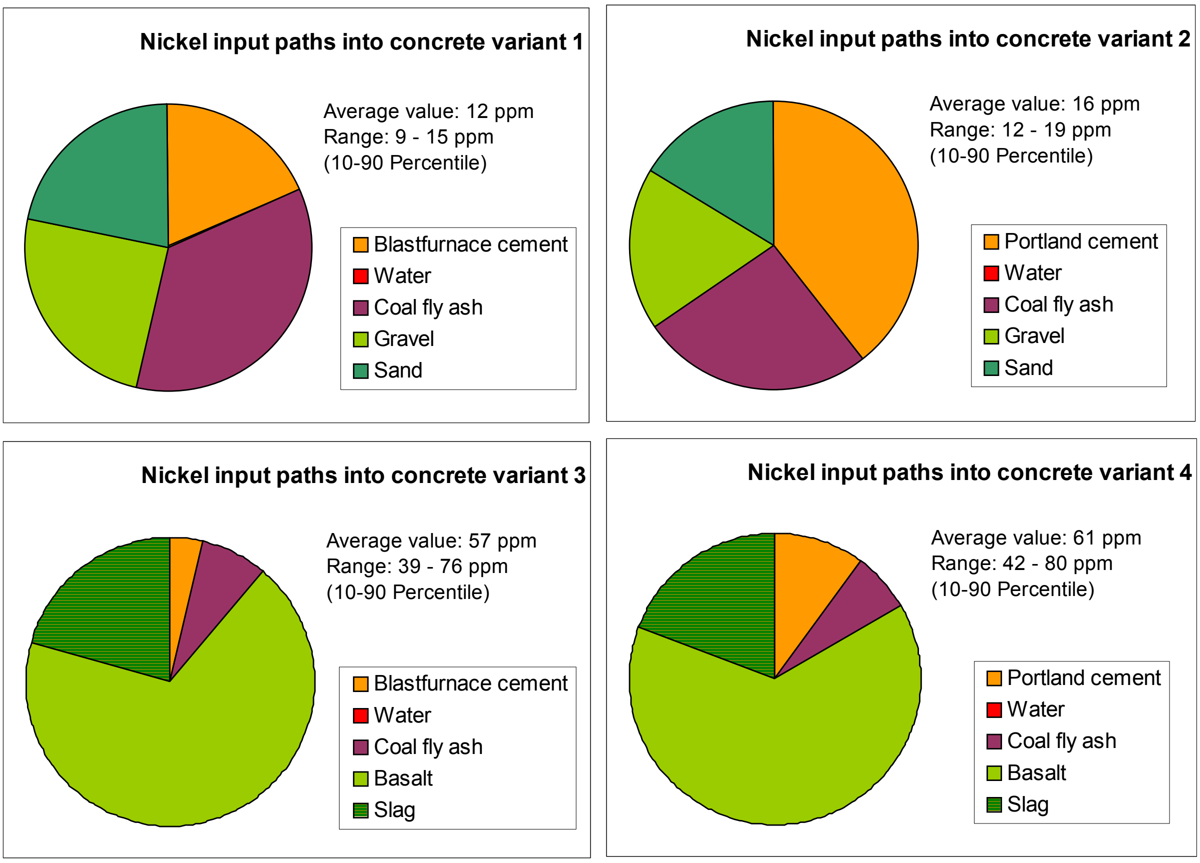


Figure 31: **Mean nickel concentrations and concentration ranges in the four concrete variants. Relative shares of the individual input materials in the total nickel concentration of concrete.**

For the concrete variants studied it may be stated that apart from cement, the aggregates basalt and slag and the additive coal fly ash, which all exhibit high trace element concentrations, contribute significantly to the total trace element concentrations. Especially for cobalt, chromium, copper, manganese, nickel, and vanadium contributions from slags and basalt, which represent large fractions of the concrete, to the total trace element concentration of concrete are of importance. However, the contributions by coal fly ash to the total concentration in concrete are not to be neglected despite the small amounts used (2%) and sometimes exceed 20% (for example, for arsenic and lead). In addition, coal fly ashes have a high specific surface area and, thus, contain trace elements in a potentially mobilisable form.

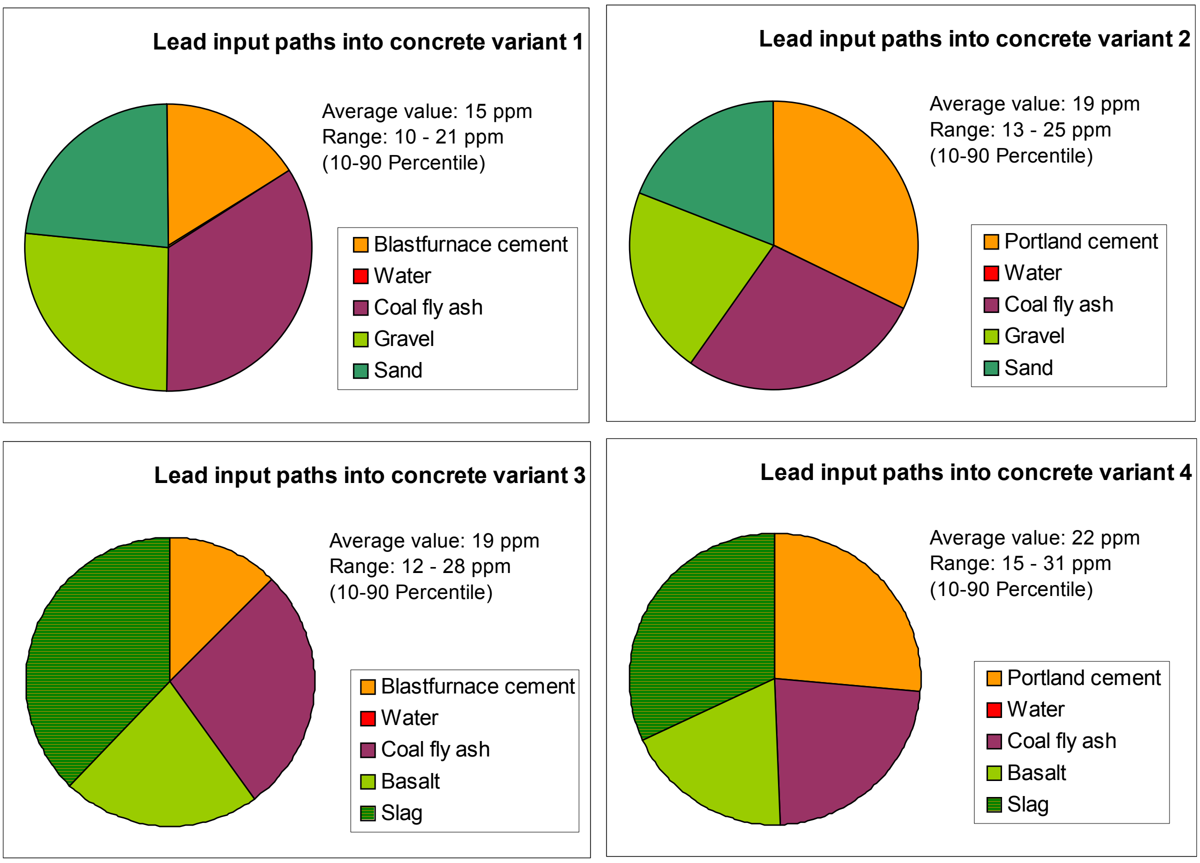


Figure 32: **Mean lead concentrations and concentration ranges in the four concrete variants. Relative shares of the individual input materials in the total lead concentration of concrete.**

2.7 A summary of the results gained by material flow analyses

The following results were obtained by material flow analyses:

The calculated mean trace element concentrations in selected types of cement and in “mixed cement” are in good agreement with the measured values.

In addition, contributions of the individual input paths to trace element transfer into clinker and different types of cement were presented. Primary raw materials were found to represent the most important input path. However, raw meal is not the only major source of the trace elements contained in clinker and cement. Also secondary input materials contribute to the trace element content of cement (top-down approach). Contributions of the individual input paths may differ considerably from trace element to trace element. Apart from secondary fuels, secondary raw materials, in particular substitute materials from iron and steel industry as well as coal fly ashes, play a major role.

By using the bottom-up approach, it was demonstrated clearly for selected scenarios that the use of waste leads to an increased concentration of **cadmium, antimony, and zinc** in cement.

The trace element content resulting from the use of waste exceeds the upper value of concentrations obtained without the use of waste. Secondary input materials were also found to have a considerable influence on the concentration of **cobalt and lead** in cement. While increased antimony and zinc concentrations in cement are attributed to the use of secondary fuels, secondary raw materials are responsible for a slightly increased concentration of cobalt, lead, and cadmium in cement. According to the calculations using the different approaches (including sensitivity calculations), the use of waste has no significant effect on the concentrations of all other trace elements investigated.

The major results obtained from the material flow analyses of the individual trace elements contained in cement are presented in table 14 in note form.

Table 14: Input paths and characteristics of various trace elements.

Arsenic	High input by primary raw materials. Coal fly ash relevant as input path. Input by primary fuels exceeds that of secondary fuels.
Cadmium	Low input by primary raw materials Secondary raw materials and fuels relevant as input paths. Influence of waste utilisation on cadmium concentration of cement clearly detectable.
Cobalt	Medium input by primary raw materials. Secondary raw materials relevant as input path. Influence of waste utilisation on cobalt concentration of cement observable, but statistically unsecured.
Chromium	Medium input by primary raw materials. Secondary raw materials relevant as input path.
Copper	Low input by primary raw materials. Secondary raw and correction materials – especially iron ore - relevant as input path. Influence of waste utilisation on copper concentration of cement observable, but statistically unsecured.
Manganese	High input by primary raw materials. Low significance of secondary materials.
Nickel	High input by primary raw materials. Coal fly ash relevant as input path. Input by oil coke exceeds that of secondary fuels.
Lead	Medium input by primary raw materials. Secondary raw materials relevant as input path. Influence of waste utilisation on lead concentration of cement observable, but statistically unsecured.
Antimony	Medium input by primary raw materials. Secondary fuels relevant as input path. Influence of waste utilisation on antimony concentration of cement clearly detectable.
Tin	High input by primary raw materials. No effect of waste utilisation on tin concentration of cement.
Thallium	Medium input by primary raw materials. Secondary fuels relevant as input path. Influence of waste utilisation on thallium concentration of cement possible but not detectable due to lack of data.
Vanadium	High input by primary raw materials. Coal fly ash relevant as input path. Input by oil coke exceeds that of secondary fuels.
Zinc	Low input by primary raw materials Secondary raw materials and fuels relevant as input paths. Influence of waste utilisation on zinc concentration of cement clearly detectable.

With respect to the input into concrete, it must be noted that apart from cement, coal fly ashes and the aggregates of basalt and slag possess high trace element contents and are relevant input paths. Use of waste in cement production will significantly affect the trace element concentrations of those concretes that are produced from trace element-depleted aggregates, such as sand and gravel. If required, a reduction of the trace element content of concrete might be achieved soonest by doing without coal fly ash, especially regarding the elements copper, nickel, lead, arsenic, and zinc.

3 Bonding, hydration, mobilisation: incorporation of trace elements in Portland cement, concrete, and their weathering products

Together with other construction materials, cement is usually further processed to a building. The potential environmental hazard due to trace elements contained in cement therefore originates from the building constructed or, after demolition, from the building rubble. Trace element transport in water or air may be airborne (dust) or occur via solutions. The period relevant to mobilisation may extend over more than 100 years. During this time, the building is exposed to different environmental impacts which may drastically change the physical and chemical properties of the concrete. Figure 33 demonstrates the complexity of these impacts using a concrete building as an example.

The following sections are intended to present the current state of knowledge on the mobility of trace elements from concrete and its components, in particular hardened cement paste. Concrete was selected, as the most important type of cement in Germany, i.e. Portland cement (CEM I), is mainly applied for the construction of concrete buildings. The share of cement in the total trace element content of various concretes has already been estimated in section 2.6.

Here, the input and incorporation of trace elements from Portland cement in concrete shall be described in detail. After this, the contribution of other trace element sources to the total amount, that can potentially be mobilised from concrete in the long term shall be estimated. Finally, long-term weathering of hardened cement paste, the weathering products generated, and the mobilisation potential of trace elements shall be investigated. In this way, critical components of concrete as well as critical chemical and physical boundary conditions that may cause a mobilisation shall be identified. Various utilisation scenarios shall be compared with the critical boundary conditions identified and evaluated. It is also analysed whether existing test methods are suited for the long-term prognosis of trace element mobilisation.

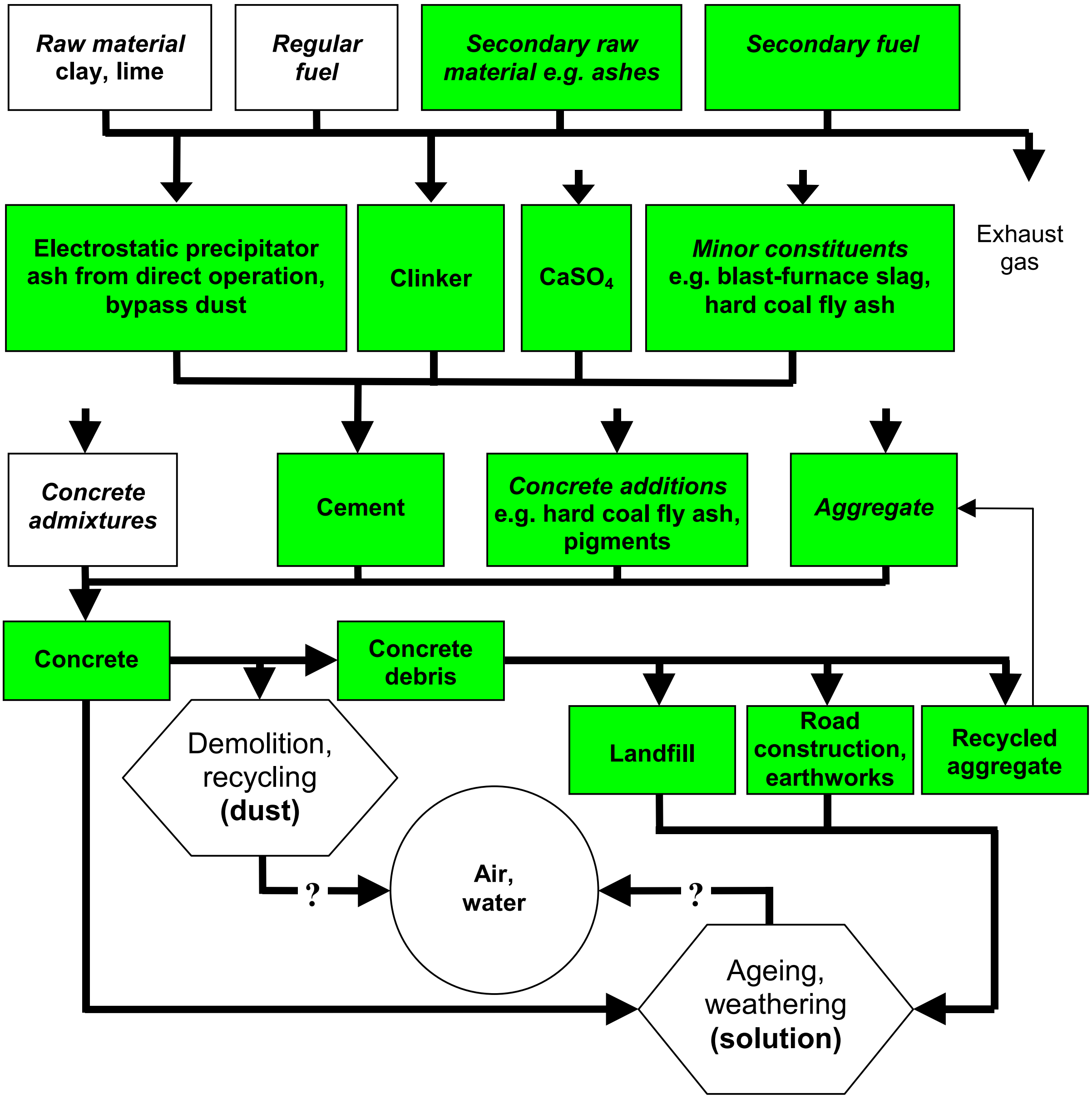


Figure 33 : **Origin, transport, and whereabouts of trace elements of a concrete building. Shaded areas might be influenced by the use of waste in cement production.**

3.1 Trace element concentrations of various cement hydrates

Within the framework of the material flow analyses (section 2), transfer of trace elements from Portland cement into concrete was determined. As was mentioned there, the results hardly allow any conclusions to be drawn with regard to potential environmental hazards, as long as the chemical mobility of the trace elements incorporated in the individual concrete components (hardened cement paste, concrete additives, aggregates, etc.) is not known.

Hardened cement paste in concrete is a composite of various trace element-containing hydrate phases (see section 1.2). As these hydrate phases have a variable susceptibility to weathering, chemical mobility of the trace elements mainly depends on the hydrate phases in which the elements are incorporated. Exact prognoses therefore do not only require the determination of absolute contents, but also an analysis of the specific concentrations of individual hydrate phases. As the various hydrates are mixed intensively and exist in extremely small crystals in real concretes, however, analysis of the trace element concentrations of individual hydrate phases has not yet been possible.

Trace element concentrations of various cement hydrates can be estimated roughly on the basis of the trace element concentrations of individual cement phases prior to hydration. Such an estimation was made under the present project (section 3.1.4). As described in section 1.2, each cement phase reacts to specific hydrates and, thus, causes the incorporated trace elements to be transferred in first approximation. Hence, the basis of later mobilisation of trace elements from cement-bound construction materials is laid already when producing the cement. However, this approach only holds as long as transport effects can be neglected, i.e. for a short time following the setting of the cement. After longer hydration times, diffusion-controlled exchange of trace elements among the different hydrate phases has to be taken into account. However, it has not yet been investigated.

To estimate the trace element concentration of individual cement hydrates (section 3.1.4) in the way outlined above, the *phase inventory of cement* (section 3.1.1), *trace element concentration of the cement phases* (section 3.1.2), and the *hydration reaction as a function of time* (section 3.1.3) have to be known.

3.1.1 Phase inventory of Portland cement

The mineralogical phase inventory of Portland cement is represented schematically in figure 34. Parts of the Portland cement, i.e. dusts and clinker granules, originate from the cement burning process. In section 2, this proportion was referred to as “cement clinker” for simplification. Other constituents, e.g. gypsum and interground additives from external sources, do not originate from the burning process. The clinker granules and dusts (electrostatic precipitator ashes from direct operation or dusts from bypasses) originating from the burning process are milled together with gypsum and external additives in the cement mill. This results in a mean grain size of about 20 µm.

Clinker granules consist of various, microscopically intergrown clinker phases (s. section 1.2). The hydraulically reacting main clinker phases C_3S, C_2S, C_3A, and C_4AF are of decisive importance in cement chemistry. Additional small amounts of secondary phases are relevant to the incorporation of trace elements.

Mineralogical composition of dusts arising in the cement plant has hardly been investigated so far. A major proportion consists of clinker minerals (CM in figure 34). In addition, dusts from bypasses in particular contain various salts, such as alkali and alkaline-earth sulphates and chlorides.

<table>
<tr><th colspan="9">Ordinary Portland Cement</th></tr>
<tr><th colspan="7">Components from the burning process, „cement clinker“ in section 3</th><th colspan="2">Other components</th></tr>
<tr><th colspan="2">Dust</th><th colspan="5">→ Clinker</th><th rowspan="2">Gypsum</th><th>Add.</th></tr>
<tr><th>Salts</th><th>CM</th><th>Minor phases</th><th>C_3S</th><th>C_2S</th><th>C_4A</th><th>C_3A</th><th>salts C_xS</th></tr>
</table>

Figure 34: **Major and minor constituents and mineralogical phase inventory of Portland cement. CM = clinker minerals. Add. = Additives.**

The sulphate carrier (mostly gypsum) and other interground additives do not originate from the burning process. When the interground additives, e.g. blast-furnace slag (bfs) or coal fly ash (cfa), react hydraulically or pozzolanically, they mainly consist of calcium-dominated glasses or crystalline calcium silicates (in figure 34 summarised as C_xS). In addition, coal fly ash contains soluble salts.

3.1.2 Bonding and concentration of trace elements in various cement phases

To determine the distribution of trace elements over various cement phases, an extensive search of national and international literature sources was accomplished. The data obtained are summarised in table A11 in the annex.

Bonding of trace elements in clinker phases

Regarding the bonding of trace elements in clinker phases, many laboratory studies were carried out on synthetic main clinker phases (C_3S, C_2S, C_3A, and C_4AF). Maximum incorporation limits were determined (s. table A11 in the annex). These maximum incorporation limits are reached in equilibrium with high partial pressures in the gas phase and, hence, cannot be compared with technical incorporation limits. However, they indicate the specific phase in which the element studied is preferably fixed crystallographically. Maximum incorporation limits mostly exceed the concentrations really observed in cement clinker by a factor of 20 at least.

Technical samples are required to find out whether an incorporation of a trace element in a clinker phase as observed on the laboratory scale is relevant in reality. Unfortunately, the analytical methods available are not suited for directly measuring the trace element incorporation in real clinkers in the technically relevant concentration range[1]. An indication of the incorporation of trace elements in clinker phases is their distribution over various material flows in the cement burning process. Trace elements not incorporated in clinker minerals are preferably released via the gas path and, therefore, supposed to be accumulated in fly ashes. To obtain an indication of trace element incorporation in technical clinkers, literature data on trace element concentrations in clinker, in cements mainly consisting of clinker, and in airborne filter dusts were collected and compared (s. table A11 in the annex).

For Portland cement, sufficient trace element analyses have been performed. However, most of them were accomplished several years ago. Data on trace element concentrations in Portland cement clinker are rare in general. Moreover, it is mostly not clear, whether clinker granules or a mixture of clinker and filter dusts has been analysed. For this reason, data on Portland cement clinker have not been used for the estimation.

Analytical data of filter dusts in literature are older and can rarely be allocated clearly to a defined plant operation mode. In most cases, it is not distinguished between the material being returned into the process or added as minor constituent. For comparison, CKD (Cement Kiln Dust) analytical data from the USA are employed. This material is not applied as interground additive. As demonstrated by table A11 in the annex, mean trace element concentrations of filter dusts and CKD hardly differ.

In table 15, individual trace elements are classified in accordance with their share in Portland cement and filter dust.

Obviously, the trace elements arsenic, tin, cadmium, lead, and thallium are accumulated in filter dust and are hardly or not at all incorporated in the main clinker phases. The same applies to mercury, a major proportion of which leaves the cement plant with the furnace offgas. In contrast to this, barium, chromium, copper, nickel, molybdenum, antimony, zinc, tellurium, beryllium, cobalt, and vanadium obviously are incorporated in the clinker. Laboratory studies with respect to the incorporation of trace elements in clinker phases yield similar results (s. table 16).

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[1] Use of synchrotron-based analysis methods would allow to determine trace element concentrations with the resolution required.

Table 15: **Distribution of individual trace elements on ordinary Portland cement (OPC) and electrostatic precipitator ash (EPA). The elements are grouped according to the quotient EPA/OPC (trace element concentration in EPA / trace element concentration in OPC). Calculation was based on the mean concentrations given in table A11 in the annex. Hg was not considered, as a major Hg fraction leaves the cement plant with the furnace offgas.**

mainly in OPC EPA/OPC <0.2	Content OPC > Content EPA EPA/OPC ∈ [0.2-0.75]	Uniformly distributed EPA/OPC ∈ [0.75-1.5]	Content EPA > Content OPC EPA/OPC ∈ [1.5-5]	mainly in EPA EPA/OPC >5
(Ti)	Ba, Cr, Cu, Ni, Mo, Sb, Zn, Te	Be, Co, V	As, Sn	Cd, Pb, Tl

Table 16: **Maximum incorporation of trace elements in clinker phases, as determined by laboratory studies at high trace element concentrations. For trace element contents of synthetic clinker phases of more than 0.5 wt.%, crystalline incorporation is assumed. In some cases, a high concentration of Cd in the clinker phases is given, but supposed to be caused by the inclusion of CdO. Grey: main clinker mineral, in which the respective trace element is preferably incorporated. Maximum concentrations of the trace elements printed in italic letters (and the concentration of Hg) are subject to drinking water regulations. In addition, trace element-rich minor phases identified in laboratory experiments and indications of a batch-wise discharge of an element with technical clinker, as found in literature, are given. For sources, see table A11 in the annex.**

EPA/OPC		C_3S	C_2S	C_3A	C_4AF	Minor phase	Batch-wise discharge
>5	Cd	-	-	-	-	(Ca,Cd)O	
	Pb	-	-			PbO	+
[1.5-5]	As					$Ca_3(AsO_4)_2$	+
[0.75-1.5]	Co				+		
	V	+	+				
[0.2-0.75]	Ba	+					
	Cr	+	+		+		
	Cu	+			+		
	Ni				+		
	Sb					$Ca_3(SbO_4)_2$	+
	Zn	+			+	ZnO	+

In some cases, trace element-rich minor phases were detected. The behaviour of some elements is not known. Indications of a batch-wise discharge of trace elements together with technical clinker suggest the formation of deposits of separate, trace element-containing minor phases in the rotary kiln. Obviously, zinc and antimony-rich deposits – possibly as ZnO or $Ca_3(SbO_4)_2$ – contribute substantially to the discharge with clinker and might cause concentration peaks. To detect these peaks, individual samples taken as a function of time should not be combined in a mixed sample contrary to today's practice. Deposits containing lead and arsenic obviously are of minor importance compared to discharge with the filter dust.

To sum up, hardly volatile trace elements in cement clinker are mainly bound in the main hydraulic clinker phases C_3S, C_2S, and C_4AF. Maximum synthetic incorporation rates of more than 1% were reported for barium, cobalt, chromium, copper, nickel, zinc, and vanadium. In fact, these elements are not enriched in fly ash (s. table 15). In addition, some trace elements may be adsorptively bound to crystal surfaces of the clinker minerals. However, this is correlated with an increased volatility. According to the investigations performed, adsorptive bonding is of particular importance to lead. So far, minor phases with high trace element contents (e.g. ZnO, $Ca_3(AsO_4)_2$) or trace element-enriched mixed crystals of clinker phases (e.g. (Ca, Cd)O) have been detected in clinkers artificially enriched with trace elements only.

Bonding of trace elements in interground additives from the burning process

In the cement burning process various dust-like materials arise, such as filter ashes and bypass dusts or hot meals. Due to their reduced thermal load, these materials tend to have higher trace element concentrations than clinker. For the integrated control and prevention of trace element loads [Europäische Kommission, 2000], the return of these materials into the production process is recommended as the "best available technique". Materials may be returned into the burning process or by using them as interground additives (= minor constituent) for the cement product. In case material cannot be recycled in this way, alternative methods may be applied. According to Sprung (1988), the interground additive is to be metered in, "such that the trace element concentration in cement in terms of magnitude corresponds to the concentration in the natural input materials, as obtained by conversion without the loss by combustion".

Bonding of trace elements varies in electrostatic precipitator ashes, bypass dusts, and hot meal. *Electrostatic precipitator ashes* consist of particulate material, such as clinker dust, intermediate products of the burning process (e.g. CaO, $CaCO_3$, $2Ca_2SiO_4 \cdot CaSO_4$), latent hydraulic glass phases, and salts (in particular alkali chlorides). Highly volatile trace elements are mainly bound adsorptively on surfaces and in salts. As compared to clinker, the concentrations of cadmium, lead, and thallium as well as of arsenic and tin are considerably increased (s. table A11 in the annex). Thallium is nearly exclusively enriched in the filter dust.

Hot meal from bypasses possesses a high free lime fraction (CaO, about 50%, [Götz-Neunhöffer et al., 2000]. In the coarsely crystalline form, it has a detrimental effect on the cement product. In the finely milled form, it may be applied as interground additive. The clinker mineral only contains about 7% of belite. More than 40% of the hot meal do not react hydraulically. No data are available with regard to the types of bonding or trace element concentrations. In contrast to this, significance of trace element input by *bypass dusts from gas bypasses* increases. Gas bypasses are increasingly installed to control the chloride content in plants using chloride-containing secondary raw materials and fuels [Sprung, 1988]. The hygroscopic dusts are separated in cyclones. They contain 20 to 30% of alkalis and up to 15% of chloride [confidential oral communication]. Nothing is known on the trace element concentrations. Their formation conditions, however, allow high concentrations to be expected. Due to the limited chloride content in Portland cement (≤ 0.10% [DIN EN 197-1]), dosage by co-grinding of chlorine bypass dusts has to be controlled precisely. For this reason and due to the bad millability, bypass dust from gas bypasses is added to other interground additives upstream of the cement mill already. Cement plants in Germany are always operated in a waste-free manner. All electrostatic precipitator ashes and bypass materials are either fed back into the process or eventually enter the cement product by direct co-grinding. In the USA, however, the raw materials applied sometimes are so rich of alkali chlorides and sulphates that the dusts have to be separated as CKD. This CKD is either disposed of or used for other purposes.

Bonding of trace elements in other cement constituents

Apart from interground additives from the burning process, various natural and technical solids as well as calcium sulphate and cement additives may be applied in the production of normal cements.

The most important interground additive in terms of quantity (4.9 million t/a (1999)) is *granulated blast-furnace slag (bfs)*. It is a main constituent of Portland slag cement and blastfurnace cement and may be added to other cements as minor constituent. Granulated blast-furnace slag is formed when producing pig iron in the blast furnace by quenching the rock melt arising there in a water bath. The composition of the rock melt is primarily dominated or set by the matrix of the ore used and by additives (e.g. lime, dolomite). When cooled down slowly in air, lumpy blast-furnace slag is generated, which is mainly used in road construction. Granulated blast-furnace slag has to consist of at least two thirds of CaO, MgO, and SiO_2, with the (MgO+CaO)/SiO_2 ratio being set to > 1. Granulated blast-furnace slag is latently hydraulic (hydraulic reaction takes place upon the presence of a reaction initiator) and consists of nearly dense glass with the fraction of the crystalline phase being limited to one third by standards. According to [Hohberg et al., 1996], trace element concentrations in general are smaller than in clinker. Own literature searches (see table A2 in the annex) yield slightly increased concentrations for mercury (0.6 ppm in granulated blast-furnace slag as compared to 0.1 ppm in clinker) and thallium (0.7 ppm in granulated blast-furnace slag as compared to 0.3 ppm in clinker). Trace elements are mainly fixed in the glass.

With 0.3 million t/a in 1999 (table A3 in the annex), *coal fly ash* is the second relevant major or minor constituent that is added from outside to the cement production process. Coal fly ashes are wastes [LAGA, 1998] that are separated in filters of coal-fired power plants. These ashes are mainly fine-grained, glassy-spherical particles (mostly hollow spheres of high porosity) with pozzolanic properties. The glass phase originates from the silicate minerals that always exists in hard coal. During entrainment, the particles are coated by highly volatile salts when cooled down. As compared to clinker, concentrations of arsenic, beryllium, cobalt, copper, nickel, lead, thallium, and vanadium as well as of cadmium, chromium, mercury, selenium, antimony, and zinc are increased considerably [Hohberg and Schießl, 1995] (s.a. table A2 in the annex). For this reason, use of coal fly ash in earthwork, road construction, landscaping, and landfill construction is controlled strictly. Total trace element concentrations usually lie in the range of the german Z1 values (reference value for solids, LAGA, 1998) for soil. Mercury concentration of fly ashes from melting furnaces is significantly increased. In the aqueous eluate concentrations of arsenic, cadmium, and chromium usually exceed the Z1 values (eluate) for soil. Sulphate concentrations by far exceed the Z2 values given for the eluate [LAGA, 1998]. Maximum permissible trace element concentrations have not yet been specified for utilisation in cement. The largest fraction of coal fly ashes is applied as concrete additive (1999: 3 million t/a, see section 3.2).

All remaining major and minor constituents added to the cement are of minor importance in terms of quantity or trace element concentration. As compared to clinker, natural *limestone* partly is slightly enriched with zinc. Rhenish trass is applied as *natural pozzolanic material* in Germany. Except for thallium, trace element concentrations in general are smaller than in clinker [Hohberg et al., 1996]. The *burned shale* applied in the state of Baden-Wuerttemberg originates from the burning of oil shale at 800°C. Compared to clinker, concentrations of cadmium, mercury, and thallium are increased. *Silica fume* is a by-product generated during ferrosilicon production by the melting of quartz sand, coal, and iron at 2000°C in the electric furnace. During this process, silica fume is condensed from the gas phase. The prevailing grain size is 0.1 μm, the specific surface area amounts to ~ 200,000 cm^2/g. The SiO_2 content amounts to 85% at least [Hohberg et al., 1996]. As far as the trace element concentrations are concerned, no investigations are known. Due to the high production temperature, however, no significant contaminations have to be expected.

Apart from the major and minor constituents already discussed, about 5% of *calcium sulphate* (as gypsum, anhydrite, semihydrate or gypsum from flue gas desulphurisation) and up to about 1% of *cement additives* are co-ground with cement. As compared to clinker, the concentrations of mercury and selenium in gypsum from flue gas desulphurisation are significantly increased in single cases [Hohberg et al., 1996]. Cement additives include e.g. milling aids (organic milling aids < 0.5%) and pigments, the fraction of which is not controlled precisely. Pigments are also applied as concrete additives to dye concrete and will be discussed in section 3.2.

3.1.3 Reaction of Portland cement phases with water as a function of time

Upon the mixing of cement with water, the various cement phases react to a variety of hydrates at varying reaction rates. Chemical fundamentals of the hydration of the most important clinker minerals C_3S, C_2S, C_3A, and C_4AF have already been described in section 1.2. Figure 35 shows the new formed phase assemblages as a function of reaction time (t0 to t3).

First, salts (e.g. Na_2SO_4 from clinker, salts from electrostatic precipitator ashes, bypass dusts, coal fly ashes), part of the C_3A and gypsum, and a small fraction of calcium from the calcium silicates are dissolved within a few minutes, until the solution is oversaturated with respect to $Ca(OH)_2$ and AFt (t0 in figure 35). Little is known on the behaviour of non-hydraulic minor phases. Then, $Ca(OH)_2$ and AFt grow from the supersaturated solution (t1) with dissolved trace elements being fixed. At the end of this period, the cement sets. After a few hours, hardening starts with the calcium silicates C_3S and C_2S being directly converted into CSH. Trace elements included in the calcium silicates are directly immobilised in CSH (t2). After about a day (t3), conversion of C_4AF into AFm starts. At the same time, also AFt is converted slowly into AFm. Hydration is completed largely after 28 days. Thorough conversion mostly is reached after several years only. Interground additives, such as granulated blast-furnace slag or glassy constituents of coal fly ash, hydrate more slowly to CSH. For these materials hydration to AFm is of minor importance [Pietersen and Bijen, 1994]. An initial grain size of 20 µm is converted within a period of five years. No structural investigations have been made with regard to the whereabouts of the high trace element concentrations that are observed in fly ashes in particular.

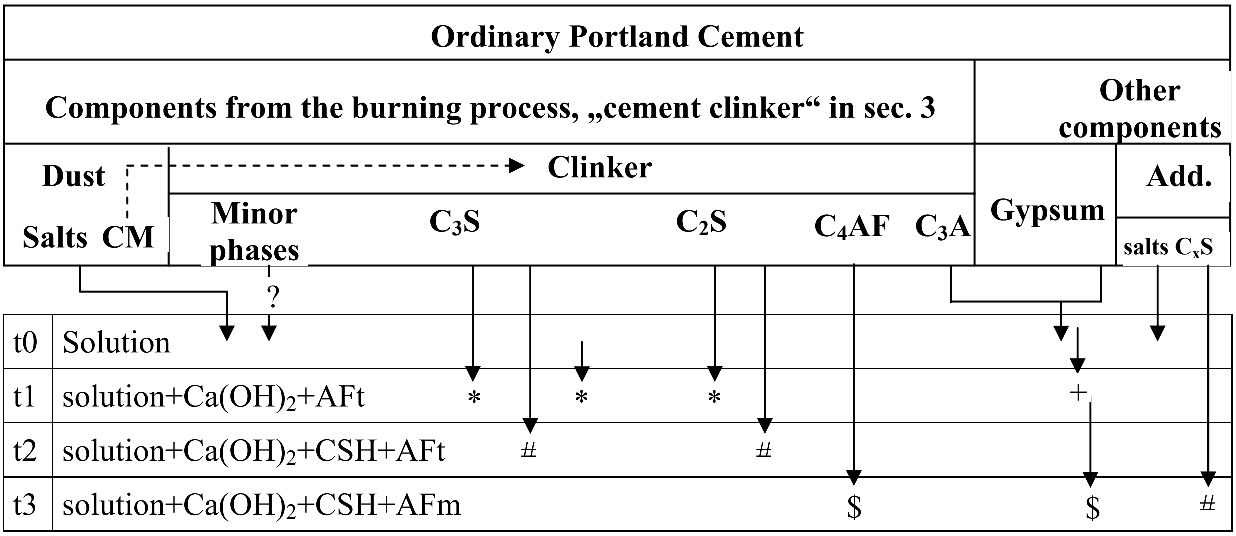

Figure 35: **Hydrate phases formed from specific cement phases as a function of time (t0 to t3). Add.: Additives. “*”: formation of $Ca(OH)_2$; “+”: formation of AFt; “#”: formation of CSH; “$”: formation of AFm.**

The reaction of bypass dust from gas bypasses with water has not yet been studied. As mentioned above, primary dissolution of salts from bypass dusts is probably due to the high alkali and chloride content. It is also not known, whether the remaining constituents of these dusts significantly contribute to the product properties of cement. According to the information provided by the Research Institute of the Cement Industry (FIZ), bypass dusts from gas bypasses mainly consist of hot meal and clinker dust. The hot meal fraction with about 7% of belite only is supposed to largely exceed the clinker dust fraction. Due to the relatively small amount of bypass dusts (estimated 100,000 t/a), this material flow may be removed and disposed of. Without knowing the trace element concentrations contained, however, it cannot be decided whether this makes sense or not.

Consequently, fresh hardened cement paste mainly consists of a mixture of three mineral groups: the hydroxides ($Ca(OH)_2$ and other hydroxides), AFt or AFm, and CSH. The trace element inventories of the hydrates are mainly taken over from the specific cement phases, as evident from the schematic representation in figure 35. In addition, non-reacted water-free main clinker phases (above all C_2S), non-hydraulic minor phases, and salts dissolved in the pore solution exist.

3.1.4 Estimation of the trace element concentration of primary hydrate phases in hardened cement paste

Table 16 shows the specific incorporation of trace elements in clinker phases. Figure 35 illustrates the transfer of these trace elements to specific hydrate phases. By combining both representations, the specific trace element concentration of the hydrate phases in young cement pastes can be derived schematically (table 17).

In particular the elements of higher volatility, namely, cadmium, lead, and arsenic exist as hydroxides or in non-hydraulic minor phases. The same has to be assumed for thallium and mercury. The low-volatile elements are incorporated partly in CSH (V, Zn, Ba, Cr, Cu) and partly in AFm (Co, Zn, Cr, Cu, Ni). This trace element distribution may change by diffusion with increasing age of the hardened cement paste. The whereabouts of the trace elements bound in the glass fractions of dusts and coal fly ashes are not known.

Table 17: Schematic representation of the transfer of trace elements mainly bound in specific cement phases to specific cement hydrates. ++: primary fixation; +: secondary fixation. cfa: coal fly ash; bfs: granulated blast-furnace slag. Italic: elements, the concentrations of which are higher in cfa than in clinker. Bold: elements, the concentrations of which are higher in cfa and bfs than in clinker.

Transfer to	Trace elements primarily bound in				
	C_3A / Gypsum		C_4AF	C_3S / C_2S	Reactive Salts cogrounded materials
	Cd, Pb, As, Tl, Hg		Co, Zn, Cr, Cu, Ni	V, Zn, Ba, Cr, Cu	*As, Be, Co, Cu, Ni, Pb, V, Cd, Cr, Se, Sb, Zn*, **Hg, Tl**
Hydroxides	++	+		(+)	++ (cfa)
AFt AFm	+	++	 ++		+ (cfa) + (cfa)
CSH				++	++ (cfa, bfs)

3.2 Trace element sources in concrete

Apart from the trace elements input from cement, concrete contains other trace element-containing constituents (see figure 33). Concrete additives and admixtures are of particular relevance in this respect. The hardened cement paste of concrete, hardened cement paste, is generated under the influence of concrete additives.

Concrete additives are additives that change the properties of concrete by chemical or physical effects. Depending on their effect, it is distinguished between concrete plasticizers, superplasticizers, air entraining agents, surfactants, retarders, accelerators, molding aids, stabilisers, chromate reducers, and recycling aids for process water. Following the start of hydration, they are partly destroyed oxidatively (organics) and partly sorbed on cement hydrate phases. In general, their trace element concentration is uncritical. Their contribution to the mobilisation of trace elements by complexation and the formation of organic colloids has not yet been settled finally.

Concrete additives represent organic or inorganic materials that are finely dispersed in the grain size < 0.125 mm and improve the specific properties of concrete. Inorganic concrete additives are a major source of trace elements. Above all, coal fly ash, silica fume, natural pozzolanic materials as well as finely ground natural rock and pigments are applied, which have already been discussed as minor constituents of the cement produced. Concrete additives partly react pozzolanically and then become an integral constituent of the hardened cement paste.

Use of coal fly ashes as concrete additive in Germany is subject to DIN 1045-2 or, in case of deviations (e.g. co-incineration of waste except for sewage sludge), the requirements given in the test certificates of the German Institute for Construction Technology (DIBt). In this case, the reference values in the eluate of power plant residues Z2 [LAGA, 1998] must be observed. In 1999 in Germany, a total of 3 million tons of coal fly ashes were used as concrete additive [vom Berg, 2002]. The hydraulic behaviour and types of bonding of trace elements (in salts and glasses) have already been described in the previous section. In general, coal fly ashes strongly contribute to the potentially mobilisable trace element concentration of concrete when used as concrete additive (see section 2.6).

As far as brown coal fly ashes are concerned, only two licenses have been issued by the DIBt for use as concrete additive (2002). The trace element concentration of brown coal fly ashes is comparatively small [BZL and DPU, 2000]. Use of silica fume that has been dealt with in the previous section as concrete additive is also permitted by the DIBt.

Finely ground pigments are applied to dye cement and concrete (prevailing grain size about 0.3 µm). Depending on the cement volume, typical pigments (e.g. a-Cr_2O_3, $CoAl_2O_3$, Fe_2O_3) are added in the range of 3 to 5%. Their approval is subject to EN ISO 787-3. Pigment admixtures partly increase the absolute trace element concentration of concrete, but are deemed to be insoluble in the long term. In concentrated acids (when incorporated e.g. in the stomach), solubility is given partly. Also the inhalation of dust-shaped particles (e.g. Cr_2O_3) may be hazardous to health. Accordingly, care has to be taken when performing surface remediation work ("sandblasting") or when breaking old concrete dyed with trace element compounds. Use of fine material from concrete reprocessing in thermal processes, which may be conceivable for the future, might mobilise trace elements from pigments and aggravate recycling. Commercially relevant trace element-containing pigments are e.g. Cu-phthalocyanines, Cr_2O_3, $(Ti,Sb,Ni)O_2$, $CoAl_2O_4$, and $ZnCo_2O_4$.

Organic concrete additives include plastic dispersions of up to 20% of the cement volume. Under certain circumstances and in particular following the reprocessing of old concrete, these may serve as nutrition for microorganisms and, hence, increase the mobility of trace elements.

General requirements to be met by concrete aggregates are outlined in DIN 4226-1 (normal and heavy weight aggregates), DIN 4226-2 (light weight aggregates), and DIN 4226-100 (recycled aggregates). Concrete aggregates are fixed in the hardened cement paste mechanically and via chemical bonding. Due to their mechanical function, they possess a small average specific surface area (in the order of about 10 – 60 cm^2/g) and, thus, a small reactivity compared to the milled minor constituents of cement. In the individual case, the specific surface area is determined by the grading curve selected, which may be composed of gravel, sand, and silt fractions.

In the lower silt fraction, nearly all silicious concrete aggregates react in a slow pozzolanic manner. In this case, trace element inventories are transferred to the hardened cement paste over very long periods of time. In contrast to this, the sand and gravel fraction behaves inertly.

Neither for light nor for heavy weight aggregates environmental compatibility investigations have been performed [Hohberg et al., 1996]. Permissible trace element concentrations are not standardised. This applies to both natural aggregates, such as sand, gravel or crushed rocks (e.g. basalt, baryte), and aggregates from technical plants. From the waste property, limits only result for granulate from slag-type furnaces (maximum permissible contents according to [LAGA, 1998]). This granulate is generated from melts that are largely liquefied in slag-type furnaces of hard coal power plants at combustion temperatures ranging from 1400 to 1700°C and quenched to glassy granules in a water bath. “Usually, arsenic and trace element concentrations cannot be detected in eluates of granules from slag-type furnaces; in general, values remain below the Z0 values of soil” [LAGA, 1998]. Additionally, the granulate does not contain any highly soluble sulphates and chlorides and, hence, may be used in earthwork, road construction, landscaping, and landfill construction without any restrictions in most cases. As compared to clinker, the absolute content of copper, nickel, vanadium, and zinc is slightly increased.

Use of ferrous and non-ferrous metallurgical slags in the building sector is subject to DIN 4301. Requirements with respect to water resources management are outlined in a revised draft version. However, these requirements refer to unbound use only, i.e. not to the use as concrete aggregate. For unbound use it is also referred to the Technical Conditions of Delivery of Mineral Materials in Road Construction [TL Min-StB, 2000], where limits of 0.1 mg/l are given for copper, lead, and zinc in the eluate only.

Ferrous metallurgical slags comprise blast-furnace slags and steel works slags. Blast-furnace slags are generated from rock melts that are produced during the production of pig iron in the blast furnace and exist in variable structures, e.g. as lumpy blast-furnace slag or granulated blast-furnace slag, depending on the cooling conditions. Their composition has already been discussed when describing granulated blast-furnace slag as a minor constituent of cement. Steel works slags are generated from rock melts arising during the production of steel. They are applied in road construction.

Non-ferrous metallurgical slags are generated from rock melts arising in the production of copper, zinc, lead, ferrochromium, and zinc oxide. Their solidification structures vary as a function of the cooling conditions. In a non-ferrous metallurgical slag studied by [Hohberg and Schießl, 1995] some trace elements are highly enriched as compared to the maximum concentrations reached in clinker (enrichment by factors of 10 (barium), 3 (chromium), 4 (cobalt), 18 (copper), and 10 (zinc)). Further details on the use of non-ferrous metallurgical slags are lacking.

Recently, the use of *recycled aggregates* from the reprocessing of building rubble in concrete has been standardised [DIN 4226-100]. In contrast to other concrete aggregates, this standard specifies the maximum elution capacity of trace elements. As today’s reprocessing plants are hardly able to separate the materials fractions forming the mixed building rubble, composition of recycled aggregates is rather heterogeneous (concrete debris, bricks, glass, etc.). Use of recycled aggregates in concrete so far has been of no relevance in terms of quantity.

Apart from the concrete components already presented, use of further substances for concrete production is discussed in literature. [Traber et al., 2000] propose to use e.g. glassy, trace element-containing slags from waste incineration as interground additive or aggregate. The hydraulic behaviour of such slags was studied by [Jovanovic, 1997]. Trace elements bound in the glass phase are incorporated particularly in CSH phases (in analogy to the behaviour of the glassy fractions of fly ashes and blast-furnace granulate). Use of such slags in concrete production would certainly result in a significant increase in the trace element concentration of the concrete.

To sum up briefly, the trace element concentration of concrete is determined by the cement fraction, on the one hand, and by concrete additives, aggregates and other admixtures, on the other. During the reaction with water, trace elements are primarily mobilised, if they are incorporated in hydraulically reactive input materials of high surface area. This applies to all cement constituents and the concrete additive coal fly ash. Depending on the reaction rate of the hydraulically reacting phase, primarily mobilised trace elements are first incorporated in hydroxides (e.g. trace elements from salts) and then in AFt, AFm, and CSH. The properties of these primary hydrate phases determine the future weathering behaviour.

When burning chlorine-containing secondary fuel in cement plants, bypass dust is increasingly produced in the gas bypasses. Eventually, this dust is co-ground with cement. The trace element load of this small material flow is not known, but possibly high. If necessary, it might be disposed of on landfills. Minor constituents and interground additives, such as coal fly ashes, sometimes considerably increase the trace element concentration of the cement product. All trace elements entering the cement from various sources as well as trace element loads from coal fly ashes used as concrete additives are sorbed, precipitated or incorporated in the hardened cement paste in the medium term. Other concrete constituents are hardly polluted or react very slowly due to their small specific surface area. Hence, they may be considered inert. Relatively large, but not mobilisable trace element concentrations are introduced into certain concretes by pigments. If such concretes will be recycled thermally in the future, such pigments might cause problems.

3.3 Medium-term mobility of trace elements from concrete

Medium-term mobility of trace elements during service life has been studied relatively well. Long-term prognoses, however, still represent an unsolved problem. The observations and test methods available nearly exclusively describe or simulate the start of the weathering process that lasts for more than 100 years. Extrapolation of these data to longer terms following demolition has not yet been backed scientifically. In the sections below the know-how available with respect to the mobility of trace elements from concrete during preparation and service life shall be summarised.

3.3.1 Release of trace elements into the mixing water

As described in section 3.1.3, highly soluble salts (alkali salts, chlorides) are mobilised first after mixing e.g. from co-ground filter dust or dusts from gas bypasses and fly ashes. Therefore, high trace element concentrations are supposed to occur in the mixing water for the first few minutes. However, these are difficult to measure. Subsequently, adsorptively (e.g. to clinker phases and interground additives) bound trace elements, such as lead, are mobilised. As the pH value of the solution increases strongly by the reaction of the main clinker phases, many trace elements are precipitated immediately as hydroxides. Unprecipitated trace elements are sorbed on their surface [Yousuf et al., 1995]. Incorporation of the elements of cadmium, chromium, thallium, and zinc from the mixing water was studied by [Seidel, 1959]. Accordingly, solubility of Cr^{6+} reaches nearly 100%, as it is not able to form a hydroxide. In contrast to this, only about 0.1% of the thallium and about 0.001‰ of cadmium or zinc remain in the solution. Unfortunately, the total contents of the cement tested are not available. According to [Hohberg and Schießl, 1995], the soluble fraction of Cr^{6+} amounts to 10 – 20%. Other special investigations of trace element concentrations of mixing water are known for chromate due to the formation of skin eczemas (“mason’s scabies”). This symptom is caused by several years of contact with cement paste[2] at Cr^{6+} concentrations of about 10 – 15 ppm in the mixing water. Individual cases, however, have also been reported at lower concentrations. To solve the chromate problem, German cement industry has undertaken to limit the soluble Cr^{6+} concentration during mixing to less than 2 ppm by adopting its regulation on “chromate-depleted cements and products”. For this purpose, chromate reducers (iron(II) sulphate) are added [Schneider and Lipus, 2002].

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[2] Processable mixture of cement and water.

3.3.2 Mobility of trace elements during service life

During the first hours of the reaction already primary hydroxides are precipitated, followed by the formation of complex phases, such as AFm and AFt as well as CSH, in which trace elements are fixed by sorption, precipitation, and crystalline inclusion. The incorporation rate has hardly been investigated so far. After about 4 weeks, the process is nearly completed. All trace elements that are immobile under alkaline conditions have been immobilised nearly completely after a few days already. Hence, the leaching rates of trace elements from cement paste very rapidly decrease to about zero. Also physical immobilisation that generally remains effective during service life contributes to the small mobilisation rates. Trace element-rich minor phases, such as CdO or HgO, are "encapsulated" in particular in CSH and, thus, protected from dissolution. Trace element mobilisation takes place mainly in a diffusion-controlled manner [van der Sloot et al., 2001].

Carbonatisation starts during service life already, driven by the high pH value of the pore solutions in concrete. By CO_2 from the air, carbonic acid is generated on the concrete surface, as a result of which the pH value of the pore solution is decreased slowly and calcium is dissolved from hardened cement paste (at first, mainly from $Ca(OH)_2$). Dissolved calcium is immediately precipitated as calcite ($CaCO_3$) in the pore volume. The carbonatisation rate strongly depends on the initial porosity and wetting of the surface. For orientation purposes, 10 mm can be assumed for a period of 20 years.

The superficially decreasing pH in principle enhances the mobilisation of many trace elements. Mobilisation of trace elements from concrete, however, also depends on the latter's physical properties. A major parameter is the primary porosity of the hardened cement paste. It is mainly influenced by the amount of water used in concrete production, the quality of homogenisation or compaction, and the concrete formula. With increasing age, primary porosity may change dramatically. For instance, it is reduced by the precipitation of calcite. As a result, velocity of the solution transport decreases, such that the mobilisation rates of the trace elements into the environment remain constant or even drop. As long as the concrete body does not exhibit any mechanical damage, trace element mobilisation is accordingly small. For normal scenarios (no access of concentrated acids, monolithic concrete of small porosity) no environmentally hazardous mobilisation of trace elements has to be expected.

It is also demonstrated by elution tests that concrete does not cause any acute hazard during service life. Following lining with concrete, mass exchange with the environment is possible only via the concrete surface by leaching, percolation, and diffusion-controlled transport.

These conditions are simulated by so-called long-term leaching tests [Hillier et at., 1999]. In such tests monolithic specimens are subjected to leaching by aqueous solutions that are exchanged several times. Due to the small porosity and the high initial pH value, the mobilisation rates of trace elements measured mostly are found to be below the detection limit. Shaking tests with water (e.g. DEV-S4) on pure cement result in too high values due to the increased surface area of the material as compared to service life (s. table 29).

3.4 Weathering and ageing of hardened cement paste during and after service life

In literature the ageing process of hardened cement paste is mostly described as carbonatisation process under the formation of calcite. To explain the behaviour of hardened cement paste during service life, this approach is sufficient. As a result of carbonatisation, $Ca(OH)_2$ is first converted into calcite. At the same time, however, e.g. the calcium content of CSH decreases. Moreover, the CSH structure changes with increasing age. This structural ageing process leads to an increased strength and possibly to an improved incorporation of trace elements. The individual processes are not known in detail.

To present the existing knowledge in a comprehensive manner, a model for the long-term weathering of hardened cement paste will be derived first in the following section. The mineral phases identified as intermediate and end products, their conversions, and their capacity of fixing trace elements shall be described. After this, the geochemical behaviour of individual trace elements shall be presented. Finally, the model shall be discussed on the basis of various scenarios after service life.

3.4.1 Model of the long-term ageing of hardened cement paste

Following primary hydration, AFm, AFt, $Ca(OH)_2$, and a calcium silicate hydrate gel, C_2SH, exist in the young cement paste. AFt is slowly converted into AFm. The pore solution has a pH value of 13 (see figure 36), i.e. it is extremely alkaline.

Any solution entering the cement paste from outside therefore acts as an acid. By the access of acids, the hardened cement paste is depleted of calcium that is first dissolved in the interstitial water. Under the impact of carbonic acid formed from airborne CO_2, calcium is precipitated immediately as calcium carbonate, which may lead to the partial closure of the pore volumes. However, acids may also originate from other sources. Sulphate-containing waters (acid rain) also dissolve calcium. The same applies to acids from biological activity. As long as $Ca(OH)_2$ exists in hardened cement paste, this phase is dissolved selectively. The pH is buffered above 12. After all $Ca(OH)_2$ has been consumed, the pH drops slowly. Calcium is now dissolved from C_2SH until a CSH gel with the composition of C_1SH (tobermorite gel) is formed at a pH of about 11 in addition to AFm and mostly $CaCO_3$. During service life, this state is reached very rarely.

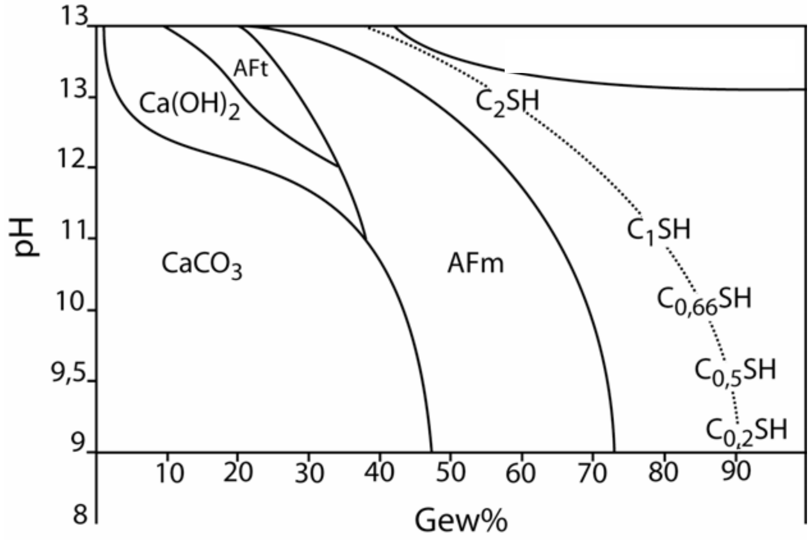

Figure 36: **Phase inventory of Portland cement pastes during diffusion-controlled acid weathering, plotted as a function of the pH value.**

Following service life, concrete is usually crushed. By demolition, porosity, grain size, and the crushing structure are modified. Mechanical and chemical weathering on the new surfaces accelerates the access of acids. As a consequence, the classical model of hardened cement paste weathering predicts a complete decomposition of C_1SH (tobermorite gel) into SiO_2 and $CaCO_3$ under a complete release of the incorporated trace elements. AFm remains unchanged until the slightly acid range is reached. It is demonstrated by own studies and data from literature, however, that weathering of C_1SH (tobermorite gel) at least passes one intermediate stage of a gyrolith-like structure $C_{0.66}SH$ (gyrolith gel) before it leads to a phase with a zeolite structure $C_{0.2}SH$ (faujasite gel). Other intermediate stages are suspected to exist.

$$C_1SH \text{ (tobermorite gel)} \rightarrow C_{0.66}SH \text{ (gyrolith gel)} \rightarrow C_{0.2}SH \text{ (faujasite gel)}$$

$$AFt \rightarrow AFm$$

Apart from the $Ca(OH)_2$ buffer at about pH 12, with the CSH-phases another buffer system exists in the cement system, which has hardly been taken into account so far and is effective between pH 11 and about 9. A third buffer, the carbonate and AFm phases only become effective in the pH range of about 5.5. If the pH drops below 9, a pH of 5.5 is reached rapidly.

Limited knowledge exists on the capacity of the various CSH gels of incorporating trace elements and on transition points of the reactions. All reactions take place in a diffusion-controlled manner. If the phases are exposed to high acid concentrations, immediate dissolution takes place without new formation of the intermediate products occurring in real concretes. The CSH buffer is "run over". Conventional laboratory tests that simulate weathering by the addition of acids (availability tests) therefore may only be considered "worst case" scenarios (s. table 29).

As mentioned, the chemical behaviour of the actual CSH gels is not known in detail. However, crystalline analogues (natural minerals) exist, for which data are available, also on trace element incorporation. In nature, C_1SH exists as tobermorite, $C_{0.66}SH$ as gyrolith, and $C_{0.2}SH$ as calcium-rich faujasite. The studies performed so far with respect to the trace element incorporation in primary cement hydrates, their weathering products, and crystalline analogues shall be summarised briefly below.

AFt (ettringite, $C_3A \cdot 3CaSO_4 \cdot 32H_2O$)

As already mentioned, AFt is thermodynamically stable at a pH in excess of 11 only. Formation of AFt starts after a few minutes and is completed after about one day. Then, slow conversion into AFm starts. According to [Gougar et al., 1996], aluminium in AFt may be replaced synthetically by Ni^{3+}, Co^{3+}, Cr^{3+}, and Ti^{3+}. Instead of sulphate, AsO_4^{3-}, CrO_4^{2-}, SeO_4^{2-}, VO_4^{-}, and MoO_4^{-} are incorporated. It is also possible to replace Ca^{2+} by Sr^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}. An immobilisation of mercury was observed. It is presumably caused by the physical inclusion of HgO. In technical systems substitution of sulphate by chromate is limited.

AFm ("monosulphate", $C_3A \cdot C\overline{S} \cdot 12H$)

AFm is formed during primary hydration already and subsequently results from the conversion of AFt. According to Pöllmann (1991), aluminium may be replaced synthetically by Cr^{3+}. Instead of sulphate, CrO_4^{2-} , MoO_4^{2-}, SeO_4^{2-}, and SeO_3^{2-} are incorporated. Moreover, Ca^{2+} may be substituted by Cd^{2+} and Zn^{2+}. In general, trace element incorporation in AFm has not yet been studied well.

$C_{2-1}SH$

Formation of C_2SH is first observed about 1 hour after mixing. The reaction is completed after about 90 days. Primary C_2SH consists of isolated silicate tetrahedra that slowly arrange in chains with increasing age of the cement. During this process, CSH is depleted of calcium and the pH of the pore solution drops. The product with its chain structure formed is referred to as C_1SH. After 20 to 30 years, 40% of dimers still exist in CSH of hardened cement paste that is located far away from the surface (i.e. groups of two tetrahedrons that are not yet connected to chains).

Fixation of trace elements in CSH has not yet been settled. Small chromium incorporation is suspected [Palmer, 2000]. At pH values in excess of 12, the C_2SH surfaces are charged positively. Cations are not sorbed, but included as hydroxides (e.g. $Ni(OH)_2$, $Zn(OH)_2$, $Pb(OH)_2$, $Cd(OH)_2$) [Gougar et al., 1996]. Sorption of anions is prevented by the high concentration of OH^- or SO_4^{2-} in the pore solution of the hardened cement paste. At a decreased pH (C_1SH), surface charge is reversed and sorption of cations, such as nickel and cobalt, increases [Glasser, 1997; Iwaida et al., 2000]. Cadmium, copper, lead, and zinc are suspected to be incorporated chemically in C_1SH [Polettini et al., 2000; Ziegler et al., 2001]. HgO is included physically in CSH.

Tobermorite, $Ca_5(Si_6O_{17}) \cdot 5H_2O$ (C_1SH analogue)

Tobermorite, a natural mineral that is also used technically e.g. in autoclaved aerated concrete, is composed of the same structural units as C_1SH gel. Incorporation of cobalt and copper instead of calcium has been confirmed [Gougar et al., 1996]. During the reaction with acids having a high trace element concentration, calcium is partly dissolved. The amorphous product fixes more than 10% of cobalt (pH = 7.4) and nickel (pH = 7.4). Lead, cadmium, and zinc are slightly sorbed only and exist as carbonates (e.g. otavite, $CdCO_3$), hydroxycarbonates, and hydroxides (pH = 6/6.8/6.5). Copper is precipitated as brochantite ($Cu_4SO_4(OH)_6$) (pH = 6.5 [Komarneni et al., 1998]). Composition of the calcium-depleted product is not known. Informations on trace element incorporation under diffusion-controlled acid access is lacking.

Gyrolith ($C_{0.66}SH$ analogue)

Gyrolith is known as a natural mineral, but also from hydrothermally treated construction materials. Incorporation of zinc in gyrolith and gyrolith gel ($C_{0.66}SH$) was confirmed by the own working group. Further investigations are not known.

Faujasite gel, $C_{0.2-0.3}SH$

In literature a calcium-containing SiO_2 gel is described as the final product of C_2SH weathering in cement (C/S about 0.2 – 0.3). Mostly, it is referred to as amorphous SiO_2 only. Data on the trace element incorporation in this phase are lacking. As demonstrated by current own activities, the phase probably possesses a strongly misarranged zeolite structure (Ca faujasite). Growth of sodium-containing faujasite from fly ash or fly ash cement pre-treated with NaOH at 40° C is known from literature [Chang et al., 1999]. With increasing synthesis temperature, faujasite is substituted by zeolite-P [Atkins et al., 1995]. In addition, another zeolite structure, chabazite, is suspected to occur. Chabazite is formed under natural conditions, e.g., during weathering of volcanic glasses. All three zeolite structures represent effective ion exchangers for trace elements (Table 18).

Table 18: Confirmed incorporation of trace elements in zeolite structures of the types faujasite, zeolite-P, and chabazite.

	Faujasite	Zeolite-P	Chabazite
Ion exchange proven for	Cs^+, Ni^{2+}, Tl^+, Cd^{2+}, Sr^{2+}, Cs^+, Rb^+ , Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}.	Li^+, Zn^{2+}, Cs^+, Sr^{2+}, Ba^{2+}, Pb^{2+}.	Pb^{2+}, Cr^{3+}, Cd^{2+}.

3.4.2 Behaviour of specific trace elements in the cement system

To estimate the behaviour of individual trace elements in the cement system on the basis of the weathering model sketched for hardened cement paste, the information given in the previous sections with regard to the fixation of trace elements in primary technical cement hydrates (section 3.1.4) and the fixation of trace elements in synthetic, pure cement hydrates and crystalline analogues (section 3.4.1) has to be taken into consideration. Furthermore, general geochemical data on the specific behaviour of trace elements in a solution at variable pH have to be taken into account. For elements, for which sufficient data exist, it can then be estimated at which pH a mobilisation into interstitial water has to be expected under diffusion-controlled conditions (see tables 19 – 28).

Arsenic

In products from thermal processes formed under moderately reducing conditions, arsenic generally exists in the form of As^{3+} opposed to As^{5+} under oxidising conditions. The toxic effect of As^{3+} is stronger. In alkaline media the species of arsenite (AsO_3^{3-} in the absence of sulphate) or arsenate (AsO_4^{3-}) are stable, depending on the redox conditions. Due to the high sulphate content of the cement system, occurrence of arsenite in hardened cement paste is improbable. In contrast to this, arsenite may originate e.g. from coal fly ashes. With decreasing pH, the arsenate ion is increasingly protonated until arsenic acid, H_3AsO_4, is formed from pH 2.

As derived in section 3.1.4, arsenic is mainly enriched in the environment of the hydroxides ($Ca(OH)_2$) following primary hydration. In case waste with a high arsenic content is bound to cement, direct precipitation of $CaHAsO_3$ is observed [Dutré and Vandecasteele, 1995]. In cement-bound materials, crystalline incorporation or physical inclusion of arsenite or arsenate compounds have not been confirmed. For ettringite substitution of sulphate by arsenate in the pure system has been described. Incorporation in AFm is conceivable, but has not yet been demonstrated. [Van der Hoek and Comans, 1994] identified arsenic in the oxidation stage of As^{5+} in coal fly ash. The observed delay in the leaching behaviour is attributed to sorption, presumably on portlandite or ettringite. In contrast to this, [Garavaglia and Caramuscio, 1994] found out that coal fly ash contains As^{3+}. The delayed leaching behaviour again is attributed to adsorption. As a whole, the mobility of arsenic as a typical negatively charged oxoanion is critical over the entire pH range. As arsenic is mainly enriched in the environment of the hydroxides ($Ca(OH)_2$), it is probably increasingly mobilised upon the consumption of the primary hydroxide buffer at pH 11 (table 19). Specific investigations are lacking.

Table 19: Known behaviour of arsenic in the cement system. Dark grey: primary cement hydrate enriched with arsenic according to section 3.1.4. Light grey: accelerated mobilisation.

As	Speciation in cement As^{5+}							
	Bonding by sorption (S), incorporation (I), encapsulation (E) to							
pH	Carbonats	Hydroxides	Sulfates	CSH	AFm	AFt	Minor phase	solution
13		$Ca(OH)_2$ S				S,I		
12		$Ca(OH)_2$ S			I?			
11					I?			?
~7					?			?
2								H_3AsO_4

Antimony

Bonding of antimony following primary hydration is not known. Possibly, it exists as $Ca_3(SbO_4)_2$. The geochemical behaviour of antimony is similar to that of arsenic. Over a wide pH range, the oxides possess a high solubility. In alkaline media a negatively charged oxoanion exists, SbO_2^-. Immobilising effects are caused by sorption on unknown cement hydrates. An incorporation in crystalline phases is not known. The toxic effect is weaker than that of arsenic.

Barium

As derived in section 3.1.4, barium is mainly enriched in CSH following primary hydration. Crystalline incorporation of barium in a hydrate phase is not known. Exchange in zeolites is conceivable. According to [Garavaglia et al., 1994], the extremely small solubility of $BaSO_4$ controls barium concentration in the elution tests (pH 11.5 to 1.2). [Cocke, 1990] assumes a coexistence of $BaCO_3$ (pH > 11.5) and $BaSO_4$ (pH < 11.5). A toxic effect of inorganic barium compounds only has to be expected at a pH of < 1.2, which is extremely improbable under natural conditions (table 20).

Table 20: Known behaviour of barium in the cement system. Dark grey: primary cement hydrate enriched with barium according to section 3.1.4. Light grey: accelerated mobilisation.

Ba	Speciation in cement Ba^{2+}							
	Bonding by sorption (S), incorporation (I), encapsulation (E) to							
pH	Carbonats	Hydroxides	Sulfates	CSH	AFm	AFt	Minor phase	solution
13	$BaCO_3$		$BaSO_4$	?				-
12	$BaCO_3$		$BaSO_4$	?				-
11			$BaSO_4$	?				-
9			$BaSO_4$	$C_{0.2}SH$ I?				-
>1			$BaSO_4$					
1								Ba^{2+}

Lead

In aqueous systems in the presence of sulphate and carbonate, lead is soluble as Pb^{2+} in extremely acid media only (table 21). However, if the sulphate concentration decreases, Pb^{2+} is dissolved at pH 5 already. In cement-bound systems lead so far has only been observed in the oxidation stage of Pb^{2+}. Nothing is known about the behaviour of Pb^{3+} and Pb^{4+}. As derived in section 3.1.4, lead is mainly enriched in the environment of the hydroxides ($Ca(OH)_2$) following primary hydration. In general, lead compounds act as retardants of cement hydration. In rare exceptional cases, however, an accelerating effect was reported. The retarding effect is attributed to the sorption of lead, presumably as hydroxide, on unreacted clinker grains.

Table 21: **Known behaviour of lead in the cement system. Dark grey: primary cement hydrate enriched with lead according to section 3.1.4. Light grey: accelerated mobilisation.**

Pb	Speciation in cement: Pb^{2+}							
	Bonding by sorption (S), incorporation (I), encapsulation (E) to							
pH	Carbonats	Hydroxides	Sulfates	CSH	AFm	AFt	Minor phase	solution
13		$Pb(OH)_2$		S, E?			PbO	
12		$Pb(OH)_2$					PbO	
11	$PbCO_3$							
9	$PbCO_3$			$C_{0.2}SH$ I?				
5	$PbCO_3$							
5-1			$PbSO_4$?					Pb^{2+} ?
<1								Pb^{2+}

It is assumed for C_2SH that lead is not incorporated, but precipitated on the surface in complex salts (hydroxides, sulphates, or carbonates) [Gougar et al., 1996; Cartledge et al., 1990; Cocke, 1990]. In elution tests lead was found to exist as $Pb(OH)_2$ in coal fly ash [Garavaglia et al., 1994]. In hydrothermal experiments under acid conditions, slight sorption of lead on tobermorite (C_1SH analogue) was observed, which led to decomposition and the formation of carbonates (at pH 5.5 or 6). Incorporation of lead in the cages of zeolites (analogues of $C_{0.2}SH$) is known.

The small solubility of lead sulphate strongly limits the potential mobility of lead during weathering of cementitious systems. If sulphate is removed, however, mobilisation has to be expected from a pH of 5 (table 21).

Cadmium

Cadmium exhibits a distinctly amphoteric geochemical behaviour. Under highly alkaline conditions (pH > 12.5), it exists as CdO_2^{2-}, under neutral and acid conditions (pH < 8) as Cd^{2+}. In-between, cadmium is precipitated as a hydroxide or carbonate. In the cement system CdO acts as a retardant. Other Cd compounds have various effects. As derived in section 3.1.4, also cadmium is mainly enriched in the environment of the hydroxides ($Ca(OH)_2$) following primary hydration. Immobilisation of cadmium at a high pH is attributed to the physical inclusion of $Cd(OH)_2$ by C_2SH. Obviously, nucleation of C_2SH and, hence, physical inclusion is accelerated by $Cd(OH)_2$ [Cartledge et al., 1990].

[Polettini et al., 2002] assume a crystal chemistry incorporation of cadmium in C_2SH without confirming it in detail. Apart from the already mentioned immobilisation as a hydroxide, formation of cadmium carbonate has already been described [Gougar et al., 1996]. In hydrothermal experiments slight sorption of cadmium on tobermorite (C_1SH analogue) was observed. However, it led to decomposition and the formation of $CdCO_3$ (otavite) (at pH 6.8 or 6.4). Incorporation of cadmium in the cages of zeolites (analogues of $C_{0.2}SH$) is known. Mobility of cadmium might be restricted strongly by the formation of $C_{0.66}SH$ during diffusion-controlled neutralisation. However, this has not yet been proved. Under neutral conditions, cadmium is considered to be mobilisable (table 22).

Table 22: Known behaviour of cadmium in the cement system. Dark grey: primary cement hydrate enriched with cadmium according to section 3.1.4. Light grey: accelerated mobilisation.

Cd	Speciation in cement Cd^{2+}							
	Bonding by sorption (S), incorporation (I), encapsulation (E) to							
pH	Carbonats	Hydroxides	Sulfates	CSH	AFm	AFt	Minor phase	solution
13				I?,E				CdO_2^{2-}
12		$Cd(OH)_2$						
11	$CdCO_3$			C_1SH I?				
10	$CdCO_3$			$C_{0.66}SH$ I?				
9	$CdCO_3$			$C_{0.2}SH$ I?				
<7-8								Cd^{2+}

Chromium

The chemical behaviour of chromium in aqueous solutions is characterised by a change of valence, on the one hand, and by an amphoteric behaviour, on the other. Under alkaline conditions (pH > 11), chromium as Cr^{6+} in the form of the chromate anion CrO_4^{2-} is highly soluble. Sorption capacity of the cement phases for Cr^{6+} is small. Soluble CrO_4^{2-} is therefore reduced technically by the addition of Fe^{2+} salts and precipitated as $Cr(OH)_3$ [e.g. Garavaglia et al., 1994].

Under acid conditions (pH < 3), chromium exists as soluble $CrOH^{2+}$ with a changed valence. The stability field of the hardly soluble Cr_2O_3 or $Cr(OH)_3$ is located in the range in-between or under slightly reducing conditions also in highly alkaline media (pH < 13.5).

As derived in section 3.1.4, chromium is mainly enriched in CSH and AFt or AFm following primary hydration. Crystal chemical incorporation of Cr^{3+} instead of Al^{3+} [Polletini et al., 2002; Glasser, 1997] and the reversible incorporation of Cr^{6+} in calcium aluminate hydrates (AFt and AFm) are possible in pure systems. In technical systems, however, the chromate anion competes with chloride, sulphate, and carbonate ions for the same lattice positions. Slight incorporation in C_2SH of Cr^{3+} instead of Si^{4+} is suspected [Gougar et al., 1996]. Incorporation of Cr^{3+} in the cages of chabazite ($C_{0.2}SH$ analogue) is known. As the solubility of Cr^{3+} is relatively small below a pH of 11, mobilisation is small during diffusion-controlled neutralisation above pH 3 (table 23).

Table 23: **Known behaviour of chromium in the cement system. Dark grey: primary cement hydrates enriched with chromium according to section 3.1.4. Light grey: accelerated mobilisation.**

Cr	Speciation in cement Cr^{6+}, Cr^{3+}							
	Bonding by sorption (S), incorporation (I), encapsulation (E) to							
pH	Carbonats	Hydroxides	Sulfates	CSH	AFm	AFt	Minor phase	solution
13		$Cr(OH)_3$		Cr^{3+} I?	Cr^{3+},Cr^{6+} I	Cr^{3+}, Cr^{6+} I	Cr_2O_3	Cr^{6+}
12		$Cr(OH)_3$		Cr^{3+} I?	Cr^{3+},Cr^{6+} I		Cr_2O_3	Cr^{6+}
11		$Cr(OH)_3$		C_1SH I?	Cr^{3+},Cr^{6+} I		Cr_2O_3	
10				$C_{0.66}SH$ I?	Cr^{3+},Cr^{6+} I		Cr_2O_3	
9				$C_{0.2}SH$ I?	Cr^{3+},Cr^{6+} I		Cr_2O_3	
<3								$CrOH^{2+}$

Cobalt

The chemical behaviour of cobalt in aqueous systems changes markedly at a pH value of about 6. Above this pH, the stability range of $CoCO_3$, $Co(OH)_2$, and Co_3O_4 is located. Under highly alkaline conditions, Co^{2+} is mobile as $HCoO_2^-$. Below pH 6, Co^{2+} also is soluble. As derived in section 3.1.4, cobalt is mainly enriched in AFm following primary hydration (table 24).

Table 24: **Known behaviour of cobalt in the cement system. Dark grey: primary cement hydrate enriched with cobalt according to section 3.1.4. Light grey: accelerated mobilisation.**

Co	Speciation in cement Co^{2+}, Co^{3+}							
	Bonding by sorption (S), incorporation (I), encapsulation (E) to							
pH	Carbonats	Hydroxides	Sulfates	CSH	AFm	AFt	Minor phase	solution
13				Co^{3+} Co^{2+} S	?	Co^{3+},Co^{2+} I	Co_3O_4	$HCoO_2^-$
12		$Co(OH)_3$		Co^{3+} Co^{2+} S	?		Co_3O_4	
11		$Co(OH)_3$		C_1SH I	?		Co_3O_4	
10	$CoCO_3$			$C_{0.66}SH$ I?	?		Co_3O_4	
9	$CoCO_3$			$C_{0.2}SH$ I?	?		Co_3O_4	
<6								Co^{2+}

The crystal chemistry substitution of Al^{3+} by Co^{3+} and Ca^{2+} by Co^{2+} in AFt is possible in pure systems. Sorption of Co on C_2SH was observed, crystalline incorporation does not take place [Gougar et al., 1996]. In contrast to this, Co^{2+} may be incorporated in tobermorite (C_1SH analogue) in large amounts. At high contents, however, the product becomes amorphous. Incorporation of Co^{2+} in the cages of faujasite ($C_{0.2}SH$ analogue) is known. Mobility of cobalt might be limited strongly by the formation of gyrolith gel ($C_{0.66}SH$) during diffusion-controlled neutralisation. At pH values below 6, mobilisation has to be expected in any case.

Copper

Solubility of copper in aqueous systems depends in particular on the amount of carbonate available. In the absence of carbonate, copper is mobile as CuO_2^{2-} at pH values in excess of about 11. Dissolution under acid conditions starts at about pH 7. Between these pH values, CuO or $Cu(OH)_2$ exists. In the presence of carbonate, copper is precipitated as malachite $Cu_2CO_3(OH)_2$ at pH values of > 7 (table 25).

Table 25: Known behaviour of copper in the cement system. Dark grey: primary cement hydrates enriched with copper according to section 3.1.4. Light grey: accelerated mobilisation.

Cu	Speciation in cement Cu^{2+}							
	Bonding by sorption (S), incorporation (I), encapsulation (E) to							
pH	Carbonats	Hydroxides	Sulfates	CSH	AFm	AFt	Minor phase	solution
13				I?	?	?		CuO_2^{2-}
12	$Cu_2CO_3(OH)_2$	$Cu(OH)_2$		I?	?			CuO_2^{2-}
11	$Cu_2CO_3(OH)_2$	$Cu(OH)_2$		C_1SH I	?		CuO	
10	$Cu_2CO_3(OH)_2$	$Cu(OH)_2$		$C_{0.66}SH$ I?	?		CuO	
9	$Cu_2CO_3(OH)_2$	$Cu(OH)_2$		$C_{0.2}SH$ I?	?		CuO	
<7								Cu^{2+}

As derived in section 3.1.4, copper is mainly enriched in AFt, AFm, and CSH following primary hydration. [Polletini et al., 2002] assume a crystal chemistry incorporation of copper in CSH without having proved this so far.

Substitution of Ca^{2+} by Cu^{2+} in tobermorite (C_1SH analogue) has been confirmed. In contrast to this, copper is not incorporated at pH 6.5 under the influence of strong acids. At high concentrations applied, copper exists as brochantite ($Cu_4SO_4(OH)_6$). Incorporation of Cu^{2+} in the cages of faujasite ($C_{0.2}SH$ analogue) is known. Also the mobility of copper might be limited strongly by the formation of gyrolith gel ($C_{0.66}SH$) during diffusion-controlled neutralisation. No investigations have been performed with respect to reactions of AFm and AFt with copper. At pH values below 7, copper mobilisation has to be expected.

In the cement system hydration is delayed by the coating of cement grains due to the addition of $Cu(OH)_2$. Also the reaction of C_3A and the crystallisation of portlandite are inhibited. [Garavaglia and Caramuscio, 1994] investigated the leaching behaviour of coal fly ash. In this case, copper existed as tenorite (CuO).

Molybdenum

In aqueous solutions molybdenum is mobile as molybdate MoO_4^{2-} over the entire pH range and as $HMoO_4^-$ in the acid range. In the cement system high concentrations of molybdate may be precipitated as $CaMoO_4$ (powellite). In ettringite (AFt) molybdate is incorporated in the pure system. In technical systems, however, no significant incorporation of molybdate takes place. In contrast to this, substantial incorporation in AFm has been confirmed [Kindness et al., 1994]. No statements can be made with regard to the general mobility during weathering.

Nickel

In aqueous systems nickel exhibits a classically amphoteric behaviour. In the pH range between 9 and 11, $Ni(OH)_2$ is stable. In the highly alkaline range, nickel exists as $HNiO_2^-$ in the dissolved form. In the neutral and acid range, Ni^{2+} exists.

As derived in section 3.1.4, nickel is mainly enriched in AFm following primary hydration. In the cement system nickel exists as Ni-Al LDH (layered double hydroxide) according to [Scheidegger et al., 2000]. Substitution of nickel by calcium in ettringite is known. [Gougar et al., 1996] assume, however, that $Ni(OH)_2$ gel is included or sorbed in C_2SH. Nickel can be incorporated in tobermorite (C_1SH analogue) in large amounts. At high concentrations and under the effect of strong acids, the product becomes amorphous. Mobility of nickel might be limited strongly by the formation of gyrolith gel ($C_{0.66}SH$) during diffusion-controlled neutralisation. However, evidence has not yet been provided. Incorporation of nickel in the cages of faujasite ($C_{0.2}SH$ analogue) is known. $NiCO_3$ always is a metastable compound. [Garavaglia and Caramuscio, 1994] detected $NiCO_3 \cdot 6\ H_2O$ in leached coal fly ash. At pH values below 8, rapid nickel mobilisation has to be expected (table 26).

Table 26: **Known behaviour of nickel in the cement system. Dark grey: primary cement hydrate enriched with nickel according to section 3.1.4. Light grey: accelerated mobilisation.**

Ni	Speciation in cement Ni^{2+}							
	Bonding by sorption (S), incorporation (I), encapsulation (E) to							
pH	Carbonats	Hydroxides	Sulfates	CSH	AFm	AFt	Minor phase	solution
13				S,E	?	I	Ni-Al-LDH	$HNiO_2^-$
12		$Ni(OH)_2$		S,E	?			
11		$Ni(OH)_2$		C_1SH I	?			
10		$Ni(OH)_2$		$C_{0.66}SH$ I?	?			
9		$Ni(OH)_2$		$C_{0.2}SH$ I?	?			
<8								Ni^{2+}

Mercury

At pH values of < 7, mercury is highly soluble as $HgCl_4^{2-}$ or Hg^{2+}. With increasing pH, HgO or mercury becomes stable, depending on the redox conditions. In the cement system mercury exists as HgO [Cocke, 1990]. HgO is included physically in CSH and AFt [Gougar et al., 1996]. With an increasing reactive surface area, mobilisation of mercury has to be expected in any case.

Selenium

In aqueous systems selenium is mobile as selenic acid or selenite (SeO_3^{2-}) over the entire pH range. When investigating the elution behaviour of fly ash, delayed mobilisation was attributed to the sorption of selenite [Van der Hoek et al., 1994]. With increasing reactive surface area, mobilisation of selenium has to be expected in any case.

Thallium

Over the entire pH range, thallium exists as Tl_2O that is highly soluble in the alkaline range and very toxic. No literature was found with regard to possible types of bonding in cement. The relatively small mobilisation rates in mixing water, however, suggest sorption on hydrate phases, presumably portlandite. Incorporation of Tl^+ in the cages of faujasite ($C_{0.2}SH$ analogue) is known. With increasing reactive surface area, mobilisation of thallium has to be expected in any case.

Vanadium

In aqueous systems vanadium is mobile as $H_2VO_4^-$, HVO_4^{2-} or VO_4^{3+} at pH values in excess of 3. In the highly acid range, VO^{2+} exists. Vanadate is slightly toxic (table 27). As derived in section 3.1.4, vanadium is mainly enriched in CSH following primary hydration. Slight incorporation in CSH, ettringite (AFt) or AFm was observed experimentally [Heimann et al., 1992]. With increasing surface area, mobilisation has to be expected from a pH value of 9 at the latest.

Table 27: Known behaviour of vanadium in the cement system. Dark grey: primary cement hydrate enriched with vanadium according to section 3.1.4. Light grey: accelerated mobilisation.

V	Speciation in cement V^{5+}							
	Bonding by sorption (S), incorporation (I), encapsulation (E) to							
pH	Carbonats	Hydroxides	Sulfates	CSH	AFm	AFt	Minor phase	solution
13				I?	I?	I?		VO_4^{3-}
12-9				I?	I?			HVO_4^{2-}
<9								$H_2VO_4^-$, VO^{2+}

Zinc

In aqueous systems zinc exhibits an amphoteric behaviour. In the pH range between 8 and 12, ZnO or $Zn(OH)_2$ is stable. At higher amounts of zinc used, concentration in the solution is limited to about 3 ppm ZnO by the precipitation of ZnO or β-$Zn(OH)_2$. $ZnCO_3$ only occurs in the neutral range at pH 7 - 8. In the highly alkaline range, zinc exists as ZnO_2^{2-} in the dissolved form. Below pH 7, Zn^{2+} exists (table 28).

As derived in section 3.1.4, zinc is mainly enriched in AFm, AFt, and CSH following primary hydration. In AFt Zn^{2+} can be incorporated for calcium. On CSH zinc is sorbed as a hydroxide or carbonate. Crystal chemistry incorporation presumably does not take place [Gougar et al., 1996]. As direct precipitant, $CaZn_2(OH)_6 \cdot 2\ H_2O$ was observed. The hydration of cement is delayed by the coating of cement grains with $Zn(OH)_2$. Zinc incorporation in $C_{0.66}SH$ was confirmed by our own working group.

Incorporation of zinc in the cages of faujasite and zeolite-P ($C_{0.2}SH$ analogues) is known. [Ziegler et al., 2001] suppose that hemimorphite $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ is formed at increased zinc concentrations. The mobility of zinc is strongly increased during diffusion-controlled neutralisation from a pH of 7.

Table 28: Known behaviour of zinc in the cement system. Dark grey: primary cement hydrates enriched with zinc according to section 3.1.4. Light grey: accelerated mobilisation.

Zn	Speciation in cement Zn^{2+}							
	Bonding by sorption (S), incorporation (I), encapsulation (E) to							
pH	Carbonats	Hydroxides	Sulfates	CSH	AFm	AFt	Minor phase	solution
13		$CaZn_2(OH)_6.2H_2O$		S,E?	?	I	$Zn_4Si_2O_7(OH)_2.H_2O$?	ZnO_2^{2-}
12		$Zn(OH)_2$		S,E?	?		ZnO	
11		$Zn(OH)_2$		C_1SH ?	?		ZnO	
10		$Zn(OH)_2$		$C_{0.66}SH$ I	?		ZnO	
9		$Zn(OH)_2$		$C_{0.2}SH$ I	?		ZnO	
7-8	$ZnCO_3$							
<7								Zn^{2+}

Tin

Tin exists as hardly soluble SnO_2 over nearly the entire pH range. Above pH 12, tin is dissolved as SnO_3^{2-}. Sn is not immobilised by CSH [Gougar et al., 1996]. Due to the small solubility of SnO_2, tin does not represent any ecological problem.

3.4.3 Estimation of the long-term mobility of trace elements from the hardened cement paste in concrete

The data collected in the previous section and the weathering model sketched allow to estimate the mobility of trace elements from the hardened cement paste of concrete. Still, this estimation is subject to a number of uncertainties. Several trace elements, such as arsenic, antimony, selenium, thallium, and mercury, are mobile at high pH values already (about 11) after the portlandite buffer has been consumed. Subsequently, the cement system is buffered by CSH between pH 11 and 9. At first, this prevents the mobilisation of vanadium, cadmium, nickel, copper, and zinc. During further neutralisation, however, these elements are mobilised rapidly in this order. Hence, their mobilisation depends on how long the CSH buffer is effective. This should be the case after demolition only, but is not known exactly. Lead and cobalt first remain immobile by the carbonate buffer. They are soluble only at smaller pH values. However, these values may well be reached in a natural environment following the dissolution of carbonate and AFm. In contrast to this, chromium, barium, and tin are largely insoluble.

Long-term experiments with regard to the transfer of trace element concentrations from concrete into soil under diffusion-controlled conditions have not yet been carried out. Such values may be calculated by geochemical modelling, provided that structural and thermodynamic data of the mineral phases described in the previous section are available, which is not the case. Previous experiments on the modelling of the weathering reactions of concrete have not met with satisfaction [HydroGeoLogic Inc., 1998; van der Sloot et al., 2001].

Description of the weathering process also shows that the test methods available do not provide any trace element concentrations that are comparable with real conditions (table 29). Long-term leaching tests only describe the behaviour of a building on the surface during service life. Leaching tests are carried out either with water (e.g. DEV S4) or with acids (availability test). The former only describe the initial stages of weathering. Acid tests simulate a “worst case” scenario, as the CSH buffer occurring during real weathering is not effective under test conditions.

Table 29: **Examples of trace element mobilisation from Portland cement, mortar or concrete according to various test methods. Concentrations in the eluate (in ppm). The reference values of disposal class 1 (Technical Instruction Municipal Waste) are given for comparison.**

	Cement		**Mortar**	**Concrete**	
	DEV-S4 CEM I 32.5 R Hohberg & Schießl (1995)	**Availability** CEM I 32.5 R pH 4 (stat.) 1h Hohberg & Schießl (1995)	**Availability** mortar with cfa pH 4 (stat.) 1h Hohberg & Schießl (1995)	**Tank test** concrete Hillier et al. (1999)	**Technical Instruction Municipal Waste** reference values of disposal class 1
As	<0.1	**0.2**	0.1	<0.005	<0.2
Ba	1.7	135	44		
Be				<0.001	
Cd	<0.1	**0.1**	**0.1**	<0.005	<0.05
Co	<0.1	1	44		
Cr	**0.8**	**34**	**3**	<0.028	<0.05
Cu	0.03	**1**	**3**		<1
Hg	<0.1	<0.1	<0.1	<0.012	<0.005
Ni	<0.1	**6**	**3**	<0.003	<0.2
Pb	**0.2**	**0.8**	**2**	<0.005	<0.2
Sb				<0.005	
Se				<0.002	
Tl	<0.1	<0.1	0.2		
V				0.06	
Zn	0.07	**44**	**35**		<2

The material flow analyses, in combination with the weathering model, allow further general conclusions to be drawn. The trace elements that may potentially be mobilised from the hardened cement paste of concrete (s. section 2.6) are comparable with concentrations in natural sediments, even when assuming that all trace elements existing in cement and fly ash and one third of the trace elements existing in the slag eventually enter the paste. Consequently, concrete is not suspected to cause any acute danger in the soil during long-term weathering. It may only be speculated about the consequences of a diffuse trace element distribution. The situation changes, if mechanisms exist, by means of which trace elements from concrete are enriched or dissolved selectively or in an accelerated manner during weathering. This issue shall be dealt with briefly for the most important scenarios in the following section.

3.5 Mobilisation scenarios for trace elements following the demolition of a concrete building

After service life, concrete is mostly crushed to varying grain sizes and either disposed of or reused as recycled construction material. By crushing, the reactive surface area is increased massively. In addition, permeability of individual broken pieces is increased by non-completed cracks.

3.5.1 Coarse fraction

The fraction of 32-4 mm may partly substitute primary aggregates in concrete. In this case, it is to be treated as primary aggregate. Hazards by an increased trace element mobilisation [FIZ, 1997] have not yet been observed.

If the broken fraction is used in road construction, however, it is exposed to additional mechanical (e.g. driving, changes of frost and thawing periods) and chemical loads (e.g. de-icing salts, nitrate from agriculture, acid rain). Both the mechanical and the chemical attack may considerably accelerate the weathering. If, in addition, an external acid source is assumed, trace element mobilisation is expected to be further increased. In this case, immobilisation of trace elements in the intermediate phases occurring during slow weathering would be aggravated at least.

In Germany, pH values of about 4 already are the rule in e.g. forest soils. At the same time, the effect of basic industrial residues emitted into forest soils can be measured already: “The lowlands in northeast Germany are characterised by tendentially higher pH values that may not be attributed to the substrate. This is explained by the comparably smaller acid depositions in the past and high emissions of basic fly ashes. Large-area immission load of forest soils also becomes obvious when studying the trace element concentrations of the humus layer. At 25% and 38% of the sites, respectively, lead and copper contents were measured, which are toxic to major soil organisms in the materials cycle of the forest” [Wolff et al., 1998]. Similar effects might occur when using concrete debris in road construction, in particular when the initial concrete had high fly ash contents. The risk of a potential uncontrolled trace element mobilisation from concrete debris used in road construction may be reduced by using this concrete in compacted bodies that are as large as possible. This issue has not yet been studied in detail.

3.5.2 Fine fraction

The fine fraction crushed from concrete in building rubble reprocessing plants is usually applied as filling material or e.g. for the construction of noise barriers. In the fine fraction the hardened cement paste proportion is strongly enriched, such that the mobilisable trace element proportion increases. Secondly, mechanical strength is lost by crushing, such that carbonatisation advances rapidly and the material loses its buffer capacity. Other damage mechanisms known from cement chemistry, such as nitrate attack (from agriculture) or ettringite or thaumasite expansion by sulphate-containing water may additionally accelerate destruction.

With an accordingly large surface area and reduced buffer capacity, also biological weathering by organisms settling on the concrete particles becomes important. Damaging of concrete drain pipes by sulphuric acid from microbiological activity is a phenomenon that has been known for a long time. The sulphuric acid results from the oxidation of hydrogen sulphide that is generated by the reduction of the sulphate contained in sewage. In case the crushed fine fraction is subjected to weathering under reducing conditions, sulphate dissolved from the hardened cement paste is available for the microbial formation of hydrogen sulphide. In contact with the oxidising zone, sulphuric acid is released. To oxidise hydrogen sulphide, an about neutral pH value is required, which is reached rapidly by carbonatisation. Also organic acids produced by some organisms cause the complete decomposition of hardened cement paste. In this connection, the increase of the organic content of concrete due to the use of organic additives is of relevance. It represents a potential source of nutrients.

The influence of biota on the trace element mobilisation from hardened cement paste has hardly been investigated so far. However, weathering of hardened cement paste may be accelerated strongly by the growth of fungi on surfaces. [Bosshard et al., 1996] studied the mobilisation of trace elements by aspergillus niger (mould) from a dried and milled fly ash of a waste incineration plant in a sucrose-containing nutrient solution (100 g/l sucrose, 1500 ppm $NaNO_3$, 500 ppm KH_2PO_4, 25 ppm $MgSO_4\ 7 \cdot H_2O$, 25 ppm KCl, pH of the nutrient solution 5.5) at 30°C. As compared to coal fly ash, the trace element contents of this fly ash were increased by the factor of 20. Aspergillus niger grew when adding up to 10 wt % of the fly ash. The pH initially increased to about 9.3. After a rest phase depending on the amount of fly ash added, production of gluconic acid started. After 16 days, a pH of about 5.5 was reached.

During this time, up to 90% of the existing cadmium, 10% of chromium, 50% of copper, 10% of nickel, nearly 100% of lead, and more than 80% of zinc were dissolved.

Long-term studies on the trace element mobilisation from crushed fine material are not available. For the reasons mentioned above, however, use of the fine fraction is rather critical.

3.5.3 Concrete dust from surface remediation – "sandblasting"

Superficial ablation of concrete buildings gives rise to a fine concrete fraction that has to be assessed in analogy to the fine material generated by crushing. In the individual case, however, this dust might be additionally loaded with trace elements.

Enrichment of trace elements on concrete surfaces in alternately moist areas was studied by [van der Wegen and van der Plas, 1994]. On a 17 year old sluice wall made of concrete, they determined the concentration gradients for copper and molybdenum from the surface down to 160 mm depth. The concrete had been produced from blastfurnace cement with a coal fly ash additive (290 kg/m^3 blastfurnace cement, 50 kg/m^3 coal fly ash, w/z = 0.55). Mean copper concentrations in the concrete (including aggregates) amounted to about 150 ppm, molybdenum concentration reached about 20 ppm. Under water, trace element mobilisation was found to take place in a diffusion-controlled manner. In the alternately moist area, two concentration peaks generated by diffusion and precipitation during drying were found, one on the surface and another one at about 20 mm depth (= boundary of the alternately moist area). Maximum copper concentrations amounted to 2500 ppm on the surface and 1800 ppm at 20 mm depth. Maximum molybdenum concentrations amounted to 75 ppm on the surface and 35 ppm at 20 mm depth.

Biological activity may also cause an enrichment of trace elements on concrete surfaces. Dyed concrete surfaces are potentially loaded with high trace element concentrations during manufacturing already.

3.5.4 Landfill disposal

In case concrete debris is disposed of on a landfill, the weathering processes as described in section 3.4 take place in principle. However, weathering may be accelerated by other building rubble that is disposed of together with the concrete debris. In particular, a sulphate attack e.g. from gypsum plaster boards is conceivable. In this case, sulphate specifically displaces anionically bound trace elements. The resulting solutions, however, are considered to be manageable on the landfill site.

In the USA, however, local groundwater contaminations were measured in the drainage water of CKD (cement kiln dust, see section 3.1.2) mono landfills in 1998 already ([HydroGeoLogic Inc., 1998], table 30). After this, further measurements were carried out by the American Portland cement Association. Unfortunately, the partly incomplete data only give a rough survey [Tetra Tech, 2002] of the number of sites, at which the MCL (Maximum Contaminant Level according to the Safe Drinking Water Act (SDWA)) or the HBN (Health Based Numbers, EPA) were exceeded. Absolute concentrations are not indicated. Some of the limit values exceeded in 2002 lie above the concentrations determined in 1998. In general, studies on the behaviour of concrete debris at landfills are reasonable.

Table 30: Trace element concentrations of the drainage water of individual CKD mono landfills [HydroGeoLogic Inc., 1998] and number of measurement values in excess of the MCL (Maximum Contaminant Level according to the Safe Drinking Water Act (SDWA)) or the HBN (Health Based Numbers, EPA) in the drainage water of CKD mono landfills, relative to the number of the reasonably (detection limit of the analytical equipment available < limit value) sampled sites [Tetra Tech, 2002].

Element	MCL (ppm) / HBN (ppm)	samples > MCL (number of reasonably sampled sites, 2002)	samples > HBN (number of reasonably sampled sites, 2002)	Downstream level at CKD landfills(1998) bold: > MCL
Ag	0.05/0.2	1(15)	1(16)	
As	0.05/0.01	6(15)	5(8)	0.0022-0.013
Ba	2/-	0(16)	-	0.23-0.75
Be	0.004/0.004	1(8)	1(9)	0.0013-0.002
Cd	0.005/-	2(14)	-	0.004-0.0025
Cr	0.1/40	1(15)	0(15)	0.004-**0.346**
Cu	1.3/1	0(12)	0(12)	
Hg (inorganic)	0.002/0.011	0(13)	0(15)	
Ni	0.1/-	3(9)	-	
Pb	0.015/0.015	6(15)	6(15)	**0.026-1.1**
Sb	0.006/0.014	3(9)	2(11)	**0.019-0.068**
Se	0.05/0.175	5(15)	1(17)	
Tl	0.002/-	2(11)	-	**0.008-0.43**
V	-/0.3	-	0(5)	
Zn	-/10	-	1(11)	

3.6 Summary

Cement is usually processed to a building together with other materials. A potential environmental hazard due to the trace elements contained in cement may result from the building constructed or, after demolition, from the building rubble, if the weathering process is accelerated. The weathering rate in particular depends on the utilisation scenario. The period relevant to a mobilisation of trace elements extends over more than 100 years. Contamination takes place in an airborne manner (dust) or via dissolution in water. Trace element mobilisation was studied using concrete as an example.

The basis of trace element mobilisation from concrete is partly laid during cement production already. Trace elements enter the cement from the burning process or via interground additives (main and minor constituents, gypsum, cement additives) added from outside. The barium, chromium, copper, nickel, molybdenum, antimony, zinc, tellurium, beryllium, cobalt, and vanadium fractions originating from the burning process are incorporated mainly in the main clinker phases of C_3S, C_2S, and C_4AF. During hardening, C_3S and C_2S pass these trace elements on to the cement hydrates CSH and AFm in first approximation. Mobilisation of these trace elements therefore depends on the stability of these cement hydrates against weathering in first approximation. During cement production, the trace elements of arsenic, copper, tin, cadmium, lead, and thallium are mainly fixed in highly soluble fractions of filter dusts or bypass dusts that are co-ground with the cement. Following hydration, they are enriched in the range of $Ca(OH)_2$. As a result, their mobilisation is influenced decisively by the stability of the hydroxides against weathering. In particular in bypass dusts high trace element concentrations are suspected. However, analytical data are not known. This material flow might be suitable for landfill disposal. The trace element fraction that enters cement via interground additives mainly originates from the coal fly ashes. As a whole, concentrations are high. Fixation in the range of $Ca(OH)_2$ is to be assumed for arsenic, tin, cadmium, lead, thallium, and mercury. All remaining trace elements originating from coal fly ash are enriched in the range of CSH following primary hydration. After longer hydration periods, diffusion-controlled exchange of trace elements between the different hydrate phases has to be taken into account, which has not been studied so far.

Trace element concentrations of concrete originate from several sources. Apart from cement, concrete additives and admixtures represent significant input paths. Of the concrete additives, coal fly ash that has already been referred to as cement constituent plays the most important role. It reacts in the same way as in cement and eventually ends up in the hardened cement paste. In individual cases, pigments may increase the absolute trace element concentration of the concrete on the surface, but they do not contribute to the mobilisable trace element inventory.

Trace element mobilisation from concrete strongly depends on its age. During mixing, potentially high trace element concentrations are mobilised. After a few minutes, however, they are fixed in newly formed hydroxides. As this process takes place in the concrete mixer already, it is of no relevance to the environment. During service life, the high buffer capacity of $Ca(OH)_2$ above pH 12 prevents trace elements from being mobilised. Under special conditions, trace elements may be enriched on the concrete surface. The long-term behaviour of trace elements was described on the basis of a weathering model developed within the framework of this project. Following the consumption of the $Ca(OH)_2$ buffer, the CSH buffer determines trace element mobilisation between pH 11 and pH 9. Due to the structural properties of CSH and the general geochemical behaviour of specific elements, however, an accelerated mobilisation of arsenic, antimony, selenium, thallium, and mercury has to be expected. As a whole, availability of data is unsatisfactory. Upon the consumption of the CSH buffer, the pH quickly drops to a value of about 6. This may lead to the rapid mobilisation of the previously CSH-bound elements of vanadium, cadmium, nickel, copper, and zinc. At pH 6, the carbonate and AFm buffer becomes effective. Only after this buffer has been consumed completely are the elements of lead and cobalt mobilised. In contrast to this, chromium, barium, and tin are largely insoluble. The long-term behaviour of the trace elements cannot be simulated simply by test methods, as the effective buffer systems are run over due to the shorter test periods. However, tests may help to study weathering under extreme conditions. For the geochemical modelling of the systems a number of essential data are missing.

In general, slow, diffusion-controlled weathering of concrete in soil does not cause any hazard to the environment. However, absolute trace element concentrations are increased. If weathering takes place under accelerated conditions, adverse impacts on the environment may occur. Various scenarios are discussed, but cannot be evaluated due to the lack of data. In earthwork or road construction, for instance, impacts other than classical weathering, e.g. also biological activity, have to be taken into account. In concrete surfaces high concentrations might occur as a result of superficial remediation work. Uncertainties exist even for material disposed of on landfills. Judging from the state of the art of reprocessing technology, however, recycling of old concrete is not expected to cause any problems.

4 Future Prospects

This section is divided into two parts. In part 4.1 (*trends concerning material flows*) recent changes of the use of raw materials and fuels in cement industry of Germany and other European countries shall be presented briefly. For Germany influence of these changes on the trace element concentration of cement shall be estimated. Furthermore, it shall be discussed how the use of secondary raw materials, fuels, and interground additives may develop further in Germany.

Part 4.2 (*research need*) describes the need for further studies in the field of material flow analyses and the mineralogical sector. This includes proposals of measurement programs that are aimed at improving the understanding of material flows in the clinker burning process and cement production.

4.1 Trends concerning material flows

4.1.1 Use of secondary raw materials and secondary fuels from 1998 to 2001

The material flow analyses carried out under this project to estimate the mean trace element concentrations in cement (s. section 2.2) refer to the raw materials and fuels consumption in 1999. In the course of the project, the amounts of raw materials and fuels used in 2000 and 2001 as well as the amounts of clinker and cement produced in these years were published by the VDZ. In order to estimate the influence of changed input quantities on the trace element concentrations of clinker and cement, it is not only required to know the trace element contents of the individual input materials, but also the specific quantities used, i.e. the consumption of input materials relative to the amount of clinker or cement produced. Table 31 presents the amounts of clinker and cement produced from 1998 to 2001 [VDZ, 2000, 2001, 2002], [BDZ, 2002].

Table 31: Clinker and cement production from 1998 to 2001 [VDZ, 2000, 2001, 2002], [BDZ, 2002].

	1998 [mill. t]	**1999** [mill. t]	**2000** [mill. t]	**2001** [mill. t]
Production of clinker	27.52	27.74	27.67	24.52
Production of cement	34.00	36.20	35.20	31.00

According to this table, clinker and cement production remained more or less constant from 1998 to 2000. In 2001, clinker and cement production decreased by about 11% as compared to 2000.

On the basis of the data given for clinker and cement production in table 31 and with the help of data on the type and amount of raw materials and fuels used from 1998 to 2001 as included in the production statistics of the VDZ [VDZ, 2000, 2001, 2002], the specific input quantities of secondary materials can be calculated (s. table 32).

Table 32: Specific input quantities (kg/t cement) of selected secondary raw materials or interground additives in Germany cement industry from 1998 to 2001 [VDZ, 2000, 2001, 2002]. *: assignment of iron ore is not clear. It may be considered both a primary and a secondary raw material.

Group	Secondary raw materials	1998	1999	2000	2001
Ca	Lime sludge, Lime refuse from industry, etc.	5.29	3.23	7.50	12.77
Si	Blast-furnace slag	2.94	4.12	4.03	3.26
Si-Al	Residues from coal preparation	0.59	0.71	0.65	0.44
Fe	Iron ore*	2.56	3.44	3.91	3.38
	Input materials from iron and steel industry	5.00	5.00	6.5	5.82
Si-Al-Ca	Metallurgical sand	135.29	144.12	152.94	136.76
	Fly ash	11.47	8.82	9.68	9.47
	Other kinds of waste	8.82	13.03	10.41	7.26
Al	Input materials from the metal industry	0.65	1.26	1.18	1.26

As compared to 1998, specific consumption of lime-containing secondary input materials is found to be increased significantly in 2001. However, these input materials are of minor relevance compared to the natural lime-containing raw materials (limestone, marl, chalk).

In the Fe group specific input quantities of “materials from iron and steel industry” in 2000 exceeded the value of 1998 and 1999 by 30%. Also the specific consumption of iron ore that cannot be assigned clearly to the primary input materials is highest in this year. It is not clear whether these high values are due to the fact that certain input materials have been assigned to other groups – since 1999, iron oxide/fly ash mixtures of the group Si-Al-Ca were assigned to the Fe group of input materials from iron and steel industry. In 2001, the specific input quantities of materials from iron and steel industry dropped to a level comparable with 1999, although the assignment had not been changed again.

As a whole, it can be noticed that the specific input quantities of secondary raw materials from 1998 to 2001 were subject to certain fluctuations, but no clear changes occurred. However, the share of secondary fuels in the total (thermal) energy input changed considerably in the past years. From 1998 to 2001, this share has practically doubled from about 16% to more than 30%. In figure 37, the shares of the individual secondary fuels in the total energy input are compared for the years of 1999 and 2001.

The significant increase in the share of secondary fuels in the total energy input from 1999 to 2001 is mainly caused by the use of meat and bone meal and by the fractions from industry and trade (BPG). While in the statistics of 1999 meat and bone meal is not indicated as a category of its own, this input material category ranks third after the fractions from industry and trade and used tyres in 2001 (s. figure 37).

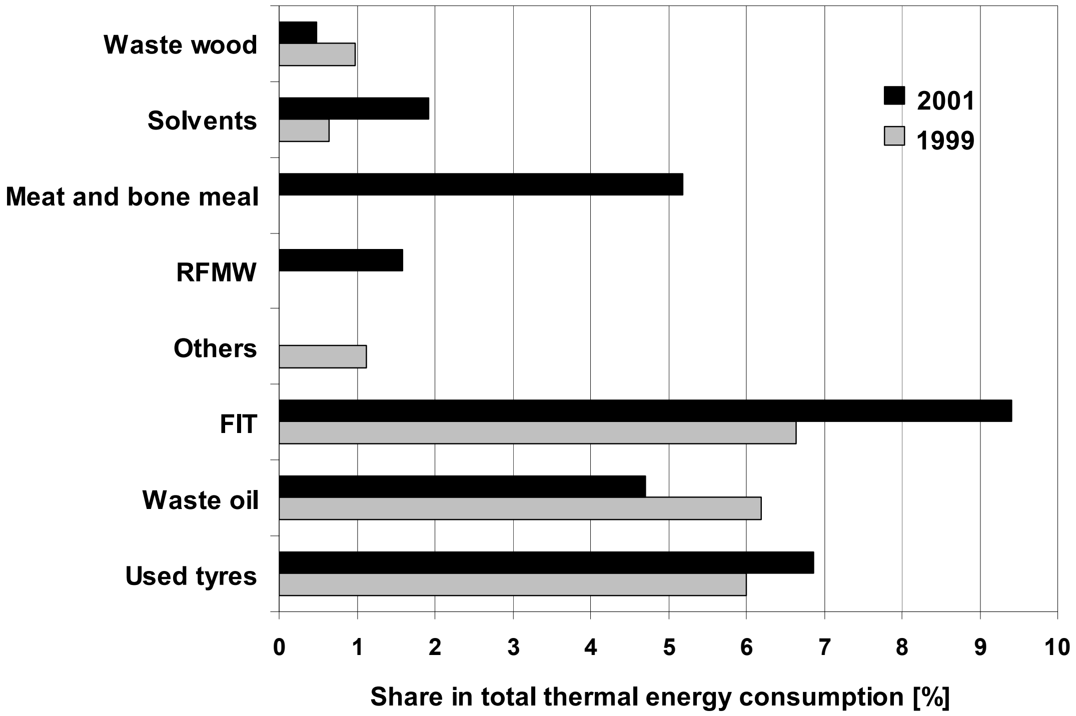

Figure 37: **Share of individual secondary fuels in the total thermal energy consumption 1999 and 2001. RFMW: reprocessed fractions of municipal wastes, FIT: fractions from industry and trade [VDZ, 2000, 2002].**

The specific amounts of secondary fuels used in 1999 and 2001 are given in table 33. In addition, the changes as compared to 1999 are obvious from the table.

As compared to 1999, use of the fractions from industry and trade increases by more than 50%, relative to a ton of clinker. The “reprocessed fractions of municipal waste” that are not indicated separately for 1999, but included in “others” are gaining importance.
The specific amount of used tyres in 2001 increased by about 14% as compared to 1999. In contrast to this, use of waste oil decreased considerably during this period. This decrease amounts to 20% relative to the amount needed to produce a ton of clinker. Among others, this is attributed to the implementation of the Waste Oil Ordinance.

Use of solvents increased considerably by more than a factor of three. Use of bleaching earth increased by the same factor, but is not listed in table 33, as this waste material plays a minor role only.

Table 33: Comparison of the specific amounts of secondary fuels used in 1999 and 2001 [VDZ, 2000, 2002].

	1999 [kg/t clinker a]	**2001** [kg/t clinker a]	**change** [%]
Waste wood	2.8	1.3	-52
Solvents	0.9	2.9	+239
Meat and bone meal		10.0	
Reprocessed fractions of municipal wastes		4.2	
Others (heating value 1999: 14 GJ/t)	3.0		
Fractions from industry and trade	11.2	17.0	+53
Waste oil	6.5	5.2	-20
Used tyres	8.5	9.7	+14

Assuming that the quantities of certain secondary fuels, e.g. fuels from production-specific wastes (BPG), permitted for use have not changed, past increase in the input quantities may well have resulted in the fact that the utilisation limits adopted for certain input materials in cement works will be reached in the near future. In 1998, for instance, the limits for the use of BPG were reached by 31% [Achternbosch and Bräutigam, 2000]. From 1998 to 2001, use of fractions from industry and trade which can be partly assigned to BPG has increased from 178,000 t to 418,000 t.

4.1.2 Effect of secondary materials used in 2001 on the trace element input into cement

Estimations of the trace element input into cement in 2001 reveal that the concentration of most trace elements in cement is slightly increased as compared to 1999, except for copper, nickel, and vanadium. However, this increase amounts to a few percent only and, hence, lies within the fluctuation range of the trace element concentrations calculated for 1999. Only for cadmium, antimony, thallium, and zinc can an increase of up to 12% be observed. While input via "primary raw materials" loses significance, secondary fuels become increasingly important, in particular used tyres and fractions from municipal, commercial and industrial waste. In contrast to this, the share of primary fuels decreases. As evident from the compositions of meat and bone meal, sewage sludge, hard coal, and brown coal in table 34, use of meat and bone meal causes comparatively small trace element concentrations in cement.

Table 34: Mean trace element concentrations of meat and bone meal, sewage sludge, hard coal, and brown coal as obtained from various sources. Data are given in ppm.

	Meat and bone meal	Sewage sludge	Coal	Brown coal
As	0.5	7	9	0.8
Cd	0.4	1.7	1.0	0.2
Co	2	10	9	1
Cr	6	80	14	3.6
Cu	26	388	18	1.8
Hg	0.2	2.3	0.3	0.2
Mn			58	77
Ni	3	34	23	3
Pb	3	250	27	3
Sb			1	0.8
Sn			4	4
Tl	0.5		1	0.1
V			39	10
Zn	140	930	63	10

Compared to other secondary fuels studied within the framework of this project, meat and bone meal exhibits the smallest trace element concentrations, the values corresponding to those of brown coal. This allows the conclusion to be drawn that trace element concentrations in cement would be increased further by doing without meat and bone meal as secondary fuel and using trace element-richer fuels instead, such as used tyres, waste oil or fractions of commercial, municipal and industrial waste.

4.1.3 Use of secondary raw materials and fuels in other European countries

Use of secondary fuels and substitute raw materials in cement industry is increasing also in other European countries.

Figure 38 shows the shares of the secondary fuels used in the 2000 total (thermal) energy input for selected countries. These data were compiled by the Spanish cement association Oficemen [Oficemen, 2003].

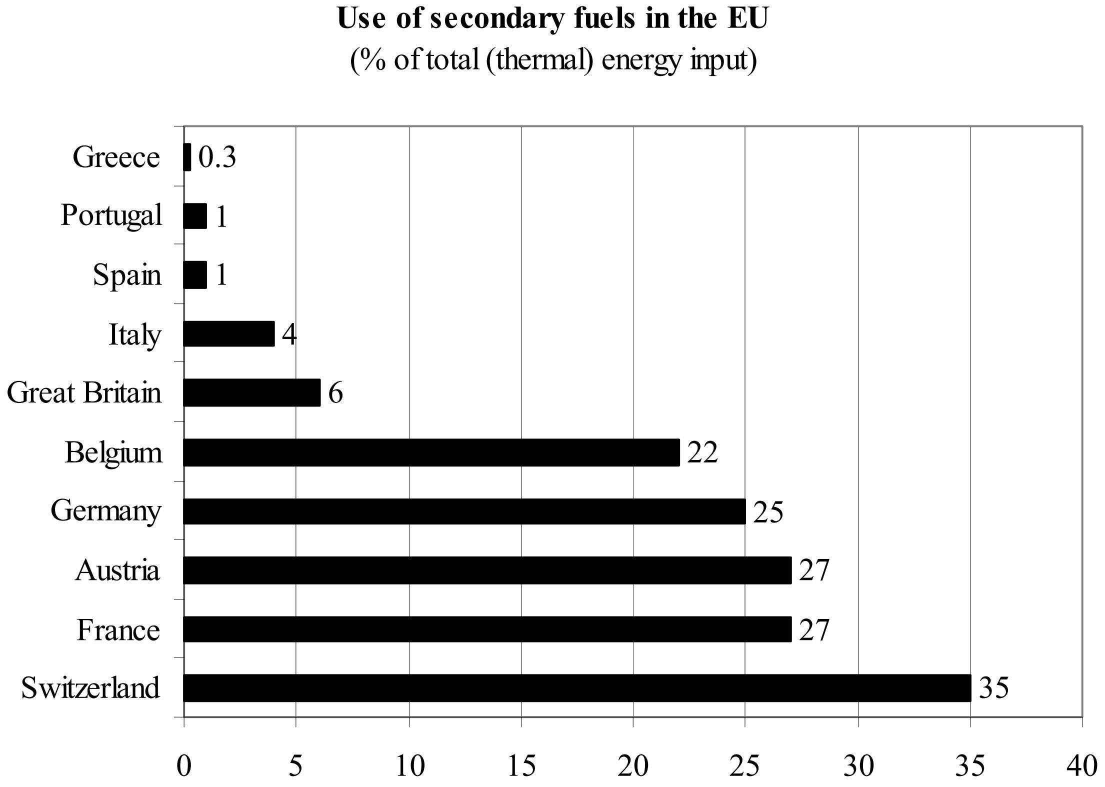

Figure 38: **Shares of the secondary fuels used in the total (thermal) energy input in various countries in 2000 [Oficemen, 2003].**

Use of secondary fuels in Austria increased from about 66,000 t in 1997 to about 145,000 t in 1999 [UBA Vienna, 2001] [Euwid, 2002b]. The specific amounts of individual secondary fuels used are obvious from figure 39.

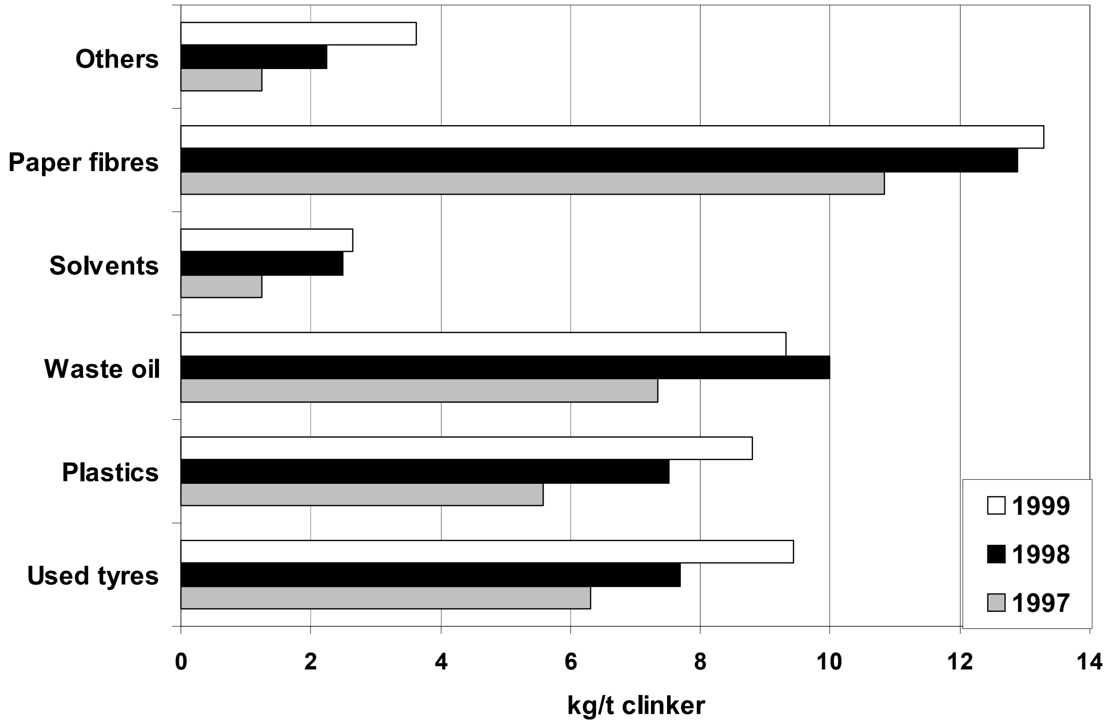

Figure 39: **Specific amounts of waste fuels used in Austria [Hackl and Mauschitz, 2001].**

In addition, seven cement works possess a license for the co-combustion of meat and bone meal [Grech, 2001]. Apart from substitute fuels, secondary raw materials are applied for clinker production in Austria. Figure 40 presents a survey of the substances and quantities used.

In Switzerland, various substitute fuels and alternative raw materials are applied in cement works. From 1999 to 2001, the share of secondary fuels in the total energy input increased from 34.4% to 41.7% [Cemsuisse, 2000, 2001]. A survey of the use of substitute fuels is given in figure 41.

The increase is mainly due to an intensified use of used tyres, solvents, and dry sewage sludge. The reason for this increased use may be the prohibition of landfill disposal in Switzerland, which became effective on 1st January 2000 [Cemsuisse, 2000]. The specific amounts of animal fats, meat and bone meal, plastics, and other materials used remained practically constant. The differences between the years 2000 and 2001 mainly result from the significant increase in the use of animal fats and meat and bone meal.

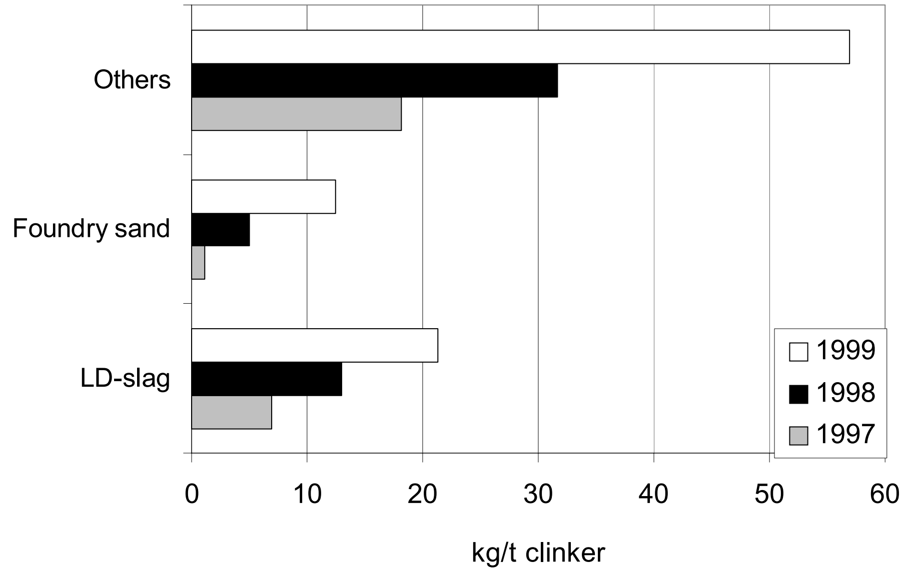

Figure 40: **Use of secondary raw materials in Austria [Hackl and Mauschitz, 2001]. LD slag: steel works slag resulting from the Linz-Donawitz process.**

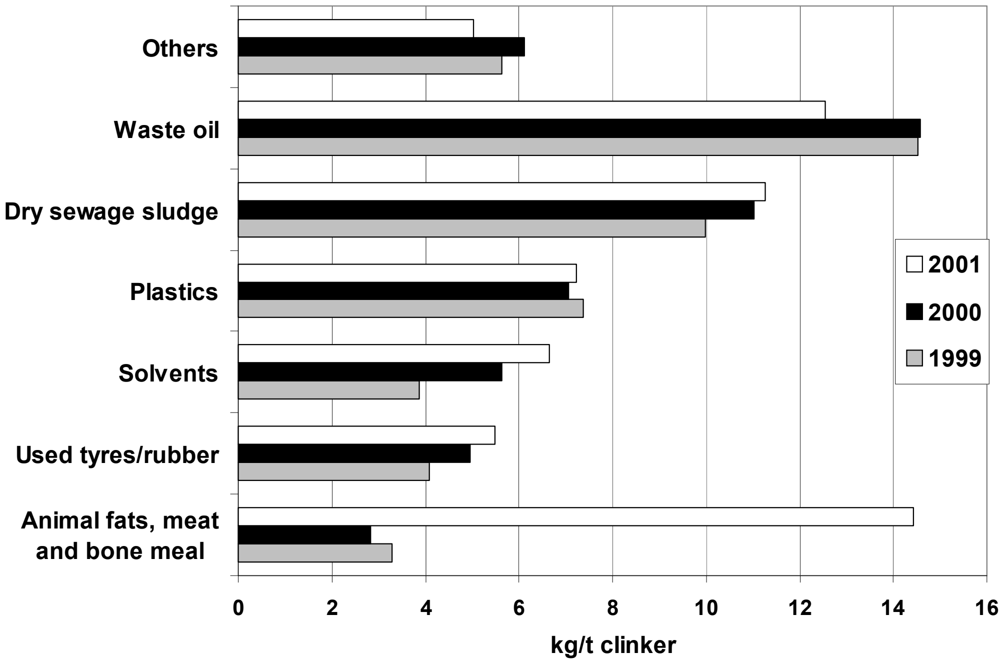

Figure 41: **Estimated use of secondary fuels in Switzerland [Cemsuisse, 2000, 2001]. Data are given in kg/t clinker.**

As alternative raw materials, material excavated in the course of tunnel construction, earth polluted by accidents, and fractions from the remediation of abondoned waste sites are employed in Switzerland among others [Cemsuisse, 2000, 2001]. Table 35 contains information on the respective quantities.

Table 35: **Use of conventional and alternative raw materials in Switzerland. Data are given in t/t clinker [Cemsuisse, 2000, 2001].**

Year	Conventional raw materials	Alternative raw materials
1999	1.54	0.08
2000	1.58	0.04
2001	1.53	0.09

Also in France, various wastes are used for the production of cement clinker. Apart from waste oil, used tyres, sewage sludge, and spent solvents, meat and bone meal and solid wastes from vehicle recycling are subjected to co-combustion. In 1999, 27% of the energy needed for clinker production were covered by wastes. The increase in the use of secondary fuels in France in the past years is reflected by figure 42 [Boyed, 2001]. While the specific energy consumption for clinker production has been constant since years, specific use of regular fuels decreases.

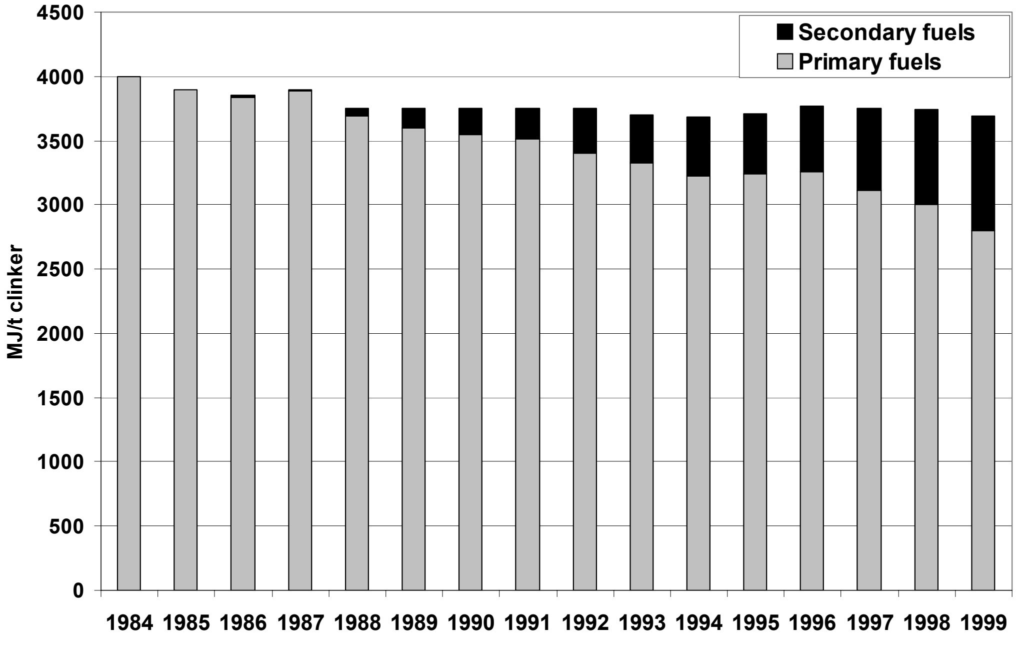

Figure 42: **Waste co-combustion in France from 1984 to 1999 [Boyed, 2001].**

The findings above demonstrate that the use of secondary raw materials and fuels increased considerably in the past years not only in Germany, but also in many other European countries. It is expected to further increase in the future.

4.1.4 Future development of waste utilisation

The trend of the last years, which shows a significant increase in the use of waste in cement production, is supposed to continue in the future.

It may be assumed that the use of used tyres will hardly change in the longer term. In contrast to this, it may well be expected that the share of waste oil will further decrease due to the Waste Oil Ordinance. However, use of waste oil in cement kilns will continue to be of a certain relevance in the future. Use of fractions of commercial, industrial and municipal waste is supposed to further increase in the future. However, new licenses will probably be required. Use of sewage sludge in cement works will gain importance, since disposal capacities are lacking due to restricted application on agriculturally used areas. This use of sewage sludge may lead to an increase in the concentration of certain trace elements, e.g. copper and lead, in clinker and cement (table 34).

Use of waste in power plants and other industrial incinerators is expected to increase. The reasons for this development vary and are partly known from the past years already. In this respect, implementation of the “TA Siedlungsabfall” (Municipal Waste Regulation) and the Waste Disposal Ordinance is of particular importance, as the disposal of untreated municipal waste on landfills will be prohibited from 2005. Consequently, municipal wastes will have to be treated in waste incineration plants or mechanico-biological waste treatment plants. As a rule, a mechanico-biological waste treatment process generates a high-calorific fraction that preferably has to be transferred to recycling according to the German Waste Management and Recycling Act. Thermal recycling is possible in both power plants and cement industry, but use of waste incinerators for this purpose is doubtful due to actual discussions on the European level. Special plants for thermal waste recycling are lacking, except for incinerators of old wood. It may be assumed that the co-incineration of the high-calorific fraction from mechanico-biological treatment facilities will increase in the future.

So far, economic branches have mainly been investigated separately for their waste management concepts and measures. Due to the links existing between different economic branches, however, this approach only covers part of the interconnected material flows. For a material flow-oriented and sustainable waste management all material flows have to be considered and optimised.

An example is the interconnection of cement industry with power plants, on the one hand, and iron and steel industry, on the other. Both power plants and iron and steel industry use waste for co-incineration. The wastes arising in these processes are partly employed in cement industry.

Fly ashes from power plants are used in cement industry as secondary raw material and interground additive. If trace element concentrations of the fly ashes are increased by co-incineration in the power plant, these increased concentrations enter the cement. Similar effects may be expected to result from the use of waste in iron and steel industry.

4.2 Research need

Improved data for material flow analyses

As explained in section 2.2, only a few data on trace element concentrations of input materials are available at the moment. Moreover, some of these data are rather heterogeneous, and representative data on the ranges and frequency distributions of concentrations hardly exist. Therefore, the database will have to be improved considerably for further investigations. This will include a more detailed differentiation of input materials in the production statistics with information being provided on their type of use (interground additive, raw material, etc.). In addition, future data collections on trace element concentrations of input materials shall contain information on the ranges and frequency distributions.

Moreover, representative data on the chemical composition of filter dust, bypass dusts, clinker, and the individual normal cements are of importance. These data should be updated and compared with each other in certain intervals so as to be able to pursue temporal variations.

Measurement programs

The measurement programs performed so far were mainly aimed at investigating the influence of the use of waste on air emissions, the quality of the cement, and on plant operation. Hardly any measurement programs exist, which focus on trace element balancing, including all input and output materials used in the production process of cement clinker. No information is available on measurement programs that also cover the cement milling stage.

So far, measurement programs have usually been carried out over a period of about two days. The samples taken were mostly combined to daily averages, with the combined sample being subjected to a representative analysis. Longer measurement campaigns were carried out for mercury. In spite of greatest care exercised in the performance of the measurement programs, the balances are subject to balancing errors that have to be attributed e.g. to the following factors:

- In particular for volatile elements in the plants, a stationary equilibrium state can hardly or not be reached at all.
- In the plant materials sources and sinks may form, which may have a strong effect during the measurement program.
- Normally, the concentrations of trace elements in the samples are very small. Many trace element concentrations are in the range of the detection limit.
- Representative sampling (in particular of coarse-grained inhomogeneous material flows) is very difficult.
- Partitioning of the samples and in particular their decomposition may considerably contribute to the total error of a materials balance.

It is also shown by the evaluation of the balances that the data frequently do not correspond to the values expected from volatility considerations. The results obtained so far provide limited information only on the distribution of trace elements over the various material flows in the plant (raw gas, clinker, filter dust, etc.). Hence, balances are of limited information content. Derivation of emission and transfer factors as measures of the share of a material of a certain material flow in the total inventory is associated with considerable uncertainties (see also the information given in the excursus: emission factors and transfer coefficients). Moreover, the derived emission and transfer factors are relevant to the plant studied only.

Despite these problems associated with the execution of measurement programs, further measurement programs should be performed, as they might provide information on the following aspects:

- The influence of sinks and sources on the material flow in the plant and on emissions has not yet been studied to a sufficient extent. In particular, the effects of sources on possible trace element concentration peaks in clinker are of considerable interest. For this purpose, measurement programs are proposed with a duration longer than two days and with the samples taken not being combined to daily averages, but analysed separately. It is not clear, to which extent the recommendations for the execution of measurement programs in waste incineration plants [Richers et al., 1999] may be transferred to cement plants.
- Chemical and mineralogical composition of the individual substances ground to cement in a cement mill are not sufficiently known. The trace element concentrations of these materials and in particular the trace element distributions over specific mineral phases are of particular relevance. During the production of cement already,

they determine the later mobilisation of trace elements from cement-bound construction materials (s. section 3.1). For this reason, material flow analyses should be complemented by mineralogical analyses. For the necessary measurements modern analytical instruments of sufficient accuracy are available.

- To obtain statistically relevant information, sampling from an increasing number of cement plants with and without waste co-incineration is desirable. Measurements should cover the trace element concentration of clinker as well as of co-ground electrostatic precipitator ashes, bypass dusts, and hot meal. In addition, temporarily resolved measurement programs are required to detect concentration peaks in the plant. Total trace element concentration should be determined in each individual sample. To identify the mineral phase inventory of the materials considered in the test program, a mineralogical analysis (microscopy, X-ray diffraction) is necessary. Trace element-rich minor phases may be detected by means of synchrotron-based X-ray diffraction. In addition, locally resolved synchrotron-based micro RFA measurements (main and trace elements) of individual mineral phases would be useful.

These programs would also allow to identify small material flows with high concentrations in the burning process, by the removal and disposal of which the total trace element concentration of cement could be reduced significantly.

Furthermore, it is recommended to study the hydraulic or at least pozzolanic behaviour of co-ground bypass dust from gas bypasses during separate reaction with water. If this behaviour is lacking, the bypass dust is lacking the major property of the cement product.

Trace element-specific phase analysis of main and minor cement constituents from external sources

In general, a phase-specific trace element analysis of the type presented in the previous section is also desirable for main and minor constituents from external sources (alien to the process). For granulated blast-furnace slag and coal fly ashes far more investigation results exist than for the material flows of the cement burning process. Still, it is reasonable to regularly check the trace element concentrations of coal fly ashes used as a minor constituent of cement or secondary raw material for possible changes (e.g. by co-incineration). If coal fly ashes are used as concrete additive, solubility of the trace elements is analysed during the licensing procedure already.

Trace element-specific phase analysis of concrete additives and admixtures

Investigation of trace element bonding in concrete additives and admixtures was beyond the scope of this study. Except for the coal fly ashes already discussed, only pigments and, possibly, smelter slags were identified to be other major trace element sources.

Behaviour of trace elements during weathering

Within the framework of this project, the lack of experimental data did not allow to reliably predict the trace element mobilisation from concrete. Such a prognosis may only be accomplished by the combined modelling of the weathering scenario, the geochemical behaviour of the cement phases, and the physical properties of the concrete.

Also in the near future, such predictions will hardly be possible due to the enormous amount of additional research needed to improve geochemical modelling. However, it can be made use of preliminary work that has already been performed with respect to the geochemical modelling of the long-term behaviour of hardened cement paste in nuclear repositories.

Geochemical models as used by geoscientists for long-term reactions describe the change in chemical properties as a function of time. Modelling requires knowledge of the fractions, trace element concentrations, and thermodynamic data of all hydrate phases contained in a specific hardened cement paste as well as of all weathering products generated. These data may only be obtained by extensive laboratory studies. Investigations are carried out first on simple systems and subsequently verified on technical systems. Available data almost exclusively refer to the service life of a building. For the time following demolition, no data are available.

Investigations to estimate the hazard potential

Trace elements enter concrete from different sources. Unless the weathering process is accelerated by specific circumstances or leads to trace element enrichments, the hazard potential as estimated today is small. However, several possible critical weathering scenarios have been identified (s. section 3.5). The relevance of these scenarios should be backed by the specific sampling of real concretes, coarsely crushed concrete, and finely crushed material, which have been exposed to weathering for several years. Additionally, the closer surroundings should be checked for trace element enrichments. Possible enrichment of trace elements in microorganisms and plants growing on contaminated concrete surfaces is deemed to be rather critical, as this would affect the beginning of the food chain.

5 Legal bases: legal and technical regulations, standards, and requirements for construction products

Cement production and the use of cement cover different legal areas with different legal regulations (standards) and other requirements having to be observed in principle. Major regulations that are of relevance to product quality shall be presented below:

- Building legislation
- Selected standards, regulations, and data sheets
- VDI regulation on emission control in cement plants
- DIBt Guideline Assessment of the effects of construction products on soil and groundwater
- Relevant parts of the federal immission control legislation, the hazardous substances legislation, and the waste management legislation

5.1 Construction legislation

5.1.1 Construction product act and Construction product directive

The Construction Product Act [BauPG] serves to implement the European Construction Product Directive [RL 89/106/EWG]. This European directive is aimed at harmonising the regulations made in the building sector with respect to the European internal market.

The Construction Product Act defines construction products as construction materials, components, and plants that are produced to be permanently installed in buildings. Moreover, pre-fabricated houses, pre-fabricated garages, and silos are understood to be construction products.

According to the requirements made in the Construction Product Act, a construction product may only be placed on the market, if its usability is proved. This means that the “installation” (building) that is to be installed in the respective building product has to meet the essential requirements listed in table 36.

Table 36: Essential requirements [BauPG].

1.	Mechanical resistance and stability
2.	Safety in case of fire
3.	Hygiene, health and the environment
4.	Safety in use
5.	Protection against noise
6.	Energy economy and heat retention.

However, the Construction Product Act does not contain any exact definition of these essential requirements. The requirements in terms of "hygiene, health, and environment" are specified in somewhat more detail in annex I of the Construction Product Directive [RL 89/106/EWG]:

> *"The construction work must be designed and built in such a way that it will not be a threat to the hygiene or health of the occupants or neighbours, in particular as a result of any of the following:*
>
> - *the giving-off of toxic gas,*
> - *the presence of dangerous particles or gases in the air,*
> - *the emission of dangerous radiation,*
> - *pollution or poisoning of the water or soil,*
> - *faulty elimination of waste water, smoke, solid or liquid wastes,*
> - *the Presence of damp in parts of the works or on surfaces within the works"*

Moreover, a construction product is deemed usable according to the Construction Product Act, if it corresponds to harmonised or acknowledged standards or deviates from these to an insignificant extent only. Usability may also be proved by a European technical license.

Usability of a construction product, as derived from harmonised and acknowledged standards, has to be proved by a conformity certificate. The Construction Product Act contains requirements made on the procedure, the declaration of conformity, and CE labelling.

Neither the Construction Product Act nor the Construction Product Directive contain any detailed requirements with regard to environmental protection or pollutant concentrations of construction products. Furthermore, the Construction Product Act does not provide any possibilities of directly limiting (national) pollutant concentrations of construction products by means of legal ordinances.

Pollutant concentrations of construction products or pollutant emission may be limited among others by standards or technical regulations. For setting up standards that are harmonised on the European level, so-called Interpretive Documents exist, in which the major requirements are formulated in detail (s. section 5.1.2).

On behalf of the Umweltbundesamt (Federal Environmental Office), the Deutsches Institut für Bautechnik (DiBt, German Institute for Construction Technology) in Berlin is currently pursuing a research project entitled “Health and Environmental Criteria in the Implementation of the EC Building Product Directive” (FKZ 20062311, duration until the end of 2003). Among others, this project is aimed at identifying the need for regulations concerning critical constituents of cement and concrete.

5.1.2 Interpretive Documents

Interpretive Documents of the European Union with respect to requirements to be met by buildings refer to the Construction Product Directive [RL 89/106/EWG]. According to Article 3 of the Construction Product Directive, major requirements to be met by buildings shall be specified in detail by the Interpretive Documents. Hence, the Interpretive Documents represent the link between the requirements made by the Construction Product Directive and the construction product standards and regulations harmonised on the European level.

In total, six Interpretive Documents exist for the major requirements listed in table 36. Here, it is restricted to the Interpretive Document “Major Requirement No. 3 Hygiene, health and the environment” [GLD-3 EU].

The essential requirements to be complied with by the buildings in terms of hygiene, health and the environment are divided into the fields of “environment inside the buildings”, “water supply”, “liquid effluents management”, “disposal of solid wastes”, and “outer environment”.

Hence, the Interpretive Document covers a very wide spectrum of impacts. On the other hand, the requirements given with respect to the fields mentioned are of rather general character.

As far as “water supply” is concerned, for instance, it is pointed out by the Interpretive Document that the health of the consumer must not be endangered by using water “for drinking and for the preparation of food, for domestic purposes or for the production of food”. Water properties must not be changed by components that get into contact with water.

Regarding the “outer environment”, the “type of requirement” only is given as follows (complete text):

> *The construction work shall not release pollutants in quantities which may impair the health and hygiene of occupants, users or neighbours.*
>
> *The requirement is concerned with the protection of people and with the prevention of any impact on the immediate environment by pollution of the air, the soil and the water. These pollutions can be generated by building materials, building services, including combustion appliances, installations.*

The proposals to limit the impacts of buildings on the outer environment and the necessary technical requirements for construction products are formulated in a similar way.

To sum up, it must be noted that the Interpretive Document no. 3 on hygiene, health and the environment does not contain any direct requirements in the form of exact pollutant lists with chemical elements or chemical compounds.

5.1.3 Building Regulations

The Building Regulations of the German states form the basis on which the building inspectorate acts. For the individual Building Regulations being largely uniform, the Model Building Regulations [MBO, 1997] exist. It is set up by working groups of the state ministers responsible for building, housing, and settlements (ARGE-BAU). Here, the Model Building Regulations shall be considered only.

The Model Building Regulations apply to construction products and constructions, in particular buildings. The law concentrates on ensuring public safety and preventing hazards for the public.

Apart from fundamental principles of licensing, approval, and control in the construction sector, the Model Building Regulations also contain requirements on the design of buildings and in particular for fire protection. According to the Model Building Regulations, use of construction products requires observation of the regulations outlined in the Construction Product Act [BauPG] and the European Construction Product Directive [RL 89/106/EWG] or compliance of the construction products with known technical rules. In this connection, the Model Building Regulations also refer to the Construction Products Lists (s. section 5.1.4).

With a few exceptions that are of no relevance to this study, the requirements given in the Model Building Regulations are formulated in a rather general manner. Precise statements with regard to e.g. the permissible pollutant concentrations of construction products are not contained in the Model Building Regulations .

5.1.4 Construction Products Lists

The Construction Products Lists are published by the German Institute for Construction Technology (DIBt) in Berlin and form the basis of the technical use of construction products for the construction of buildings. From the Construction Products Lists, it is also obvious in principle which construction products require an additional approval. At the moment, three lists, including several parts, exist.

Construction Products List A consists of a total of three parts and defines technical rules for construction products (part 1). In addition, Construction Products List A lists construction products, for which no acknowledged rules of technology exist or construction products that may be assessed according to acknowledged test procedures (part 2). The third part of Construction Products List A refers to designs for the construction of walls, ceilings, etc.

Construction Products List B is divided into two parts and lists construction products that have been granted a CE label and may be put in circulation according to the requirements specified by the European Union.

The construction products listed in Construction Products List C only have to be of normal inflammability according to building supervision requirements.

Under “construction products for concrete and reinforced concrete construction”, running number 1.1 “bonding agents”, Construction Products List A, part 1, contains various DIN standards from the system of standards 1164 for cement (s. section 5.2.2), complemented by references to various annexes of the Construction Products List. These annexes do not refer to constituents, but only to certification and labelling.

Construction Products List B, part 1, refers under running number 1.1.1.1 “normal cement when delivered by a producer to the user or middleman”. Here, the standards DIN-EN 197-1 and DIN-EN 197-2 are mentioned, which shall be presented in section 5.2.1.

5.2 Standards, regulations, and data sheets

5.2.1 DIN-EN system 197

The standards that are of paramount importance to the composition of cements form part of the DIN-EN 197 system of standards. This system of standards consists of three parts and serves to standardise cement in Europe. The standard DIN-EN 197-1 [DIN EN 197-1] entitled "Cement, Part 1: Composition, Requirements, and Conformity Criteria of Normal Cement" has been effective in Germany since April 1, 2001 [VDZ, Tätigkeitsbericht].

The standard DIN-EN 197-1 comprises definitions and explanations for 27 different types of cement as well as requirements with respect to the (chemical) composition and other properties. Compared to the old German standard, the new DIN-EN 197-1 standard covers more than twice as many types of cement. Of the 27 standardised types of cement, six are relevant in Germany, their share in total cement delivery reaching 98% [VDZ, Tätigkeitsbericht].

Depending on the type of cement, the DIN-EN 197-1 standard contains requirements with respect to the loss on ignition, insoluble residue, sulphate content, and pozzolanic behaviour. For all types of cement the chloride content is limited to less than 0.1%. Blastfurnace cements may contain higher actual chloride concentrations, for pre-stressed concrete applications smaller concentrations might be necessary.

Further requirements with respect to the chemical composition result from the main constituents specified for the 27 types of cement. These main constituents include Portland cement clinker, granulated blast-furnace slag, pozzolanic materials, coal fly ash, burned shale, limestone, and silica dust. The requirements in terms of the chemical composition are restricted to the oxides of calcium, silicon, aluminium, and iron, which are of relevance to the setting behaviour. The DIN-EN 197-1 standard does not include any precise requirements with regard to trace element concentrations or the content of other pollutants.

Minor constituents comprise selected inorganic natural mineral substances, inorganic mineral substances originating from clinker production or materials which may also be major constituents. Minor constituents, the total proportion of which must be below 5% in cement [DIN-EN 197-1], do not have to fulfil any concrete requirements with respect to their chemical composition. However, they must not adversely affect the water consumption of cement and the properties of concrete and mortar.

The DIN EN 197-2 standard [DIN EN 197-2] entitled "Cement, Part 2: Conformity Evaluation" contains further requirements with regard to the verification and proof of cement quality, including certification by a certification office.

For special applications in the construction sector, limitation of the hydration heat of cement may be reasonable. Such requirements are given by the DIN EN 197-3 standard "Cement, Part 3: Composition, Requirements, and Conformity Criteria for Normal Cements of Low Hydration Heat” [DIN EN 197-3]. The requirements made on the chemical composition and on the mechanical and physical properties of the standardised cements of low hydration heat correspond to the requirements given in the DIN EN 197-1 standard.

5.2.2 DIN system 1164

In the past, the DIN 1164 system of standards with several parts determines the national requirements for cement. Due to the adoption of European standards, certain parts of the 1164 DIN system of standards had to be revised. The requirements to be met by special types of cement, including conformity criteria, are given by the currently valid DIN 1164[3] [DIN 1164] with DIN EN 197-1 being taken into account. These special types of cement comprise cement of low hydration heat, cement of high sulphate resistance, and cement of low effective alkali content.

As far as chemical composition is concerned, the C_3A content, the aluminium oxide fraction, and the Na_2O equivalent fraction covering the chemical elements of sodium and potassium are specified.

Other parts of the DIN 1164 system of standards include requirements for analytical investigations. DIN 1164, part 8 [DIN 1164-8] describes the method of determining the hydration heat of various types of cement. Determination of the fractions of granulated blast-furnace slag and trass in various types of cement is specified by DIN 1164, part 31, dated March 1990 [DIN 1164-31].

The standards DIN 1164, 1164 - part 8, and DIN 1164 - part 31 do not contain any special requirements for the production process of the various types of cement.

5.2.3 DIN-EN system 196

The DIN-EN 196 system of standards entitled “Test Procedures for Cement” presently comprises ten parts, with sometimes draft versions being available only. The individual parts of the system of standards refer to chemical analysis of cement with its constituents (clinker, granulated blast-furnace slag), the determination of the fineness of grinding or to cement sampling methods. Another part of the system of standards specifies the procedure of determining chloride, carbon dioxide, and alkali metals.

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[3] Together with DIN EN 197-1 and DIN EN 197-2, DIN 1164 as amended in November 2000 with the new title of “Cement with Special Properties – Composition, Requirements, Conformity Criteria” replaces the DIN 1164-1 (status: October 1994) and DIN 1164-2 (status: November 1996).

Those parts of the DIN EN 196 standard, which have been taken into consideration, are listed separately in the references. However, they do not contain any special requirements with respect to the use of waste or secondary raw materials.

5.2.4 Standards relating to concrete

The specification, properties, production, and conformity of concrete are subject to the DIN EN 206-1 standard [DIN EN 206-1] on the European level. This standard allows for national rules of application as given by the DIN 1045-2 [DIN 1045-2] and DIN EN 206-1 standards.

Application of DIN EN 206-1 requires product standards or similar regulations for the individual concrete constituents, such as cement and additives, as well as standards for concrete test procedures. The relations between DIN EN 206-1 and other standards are illustrated by figure 43.

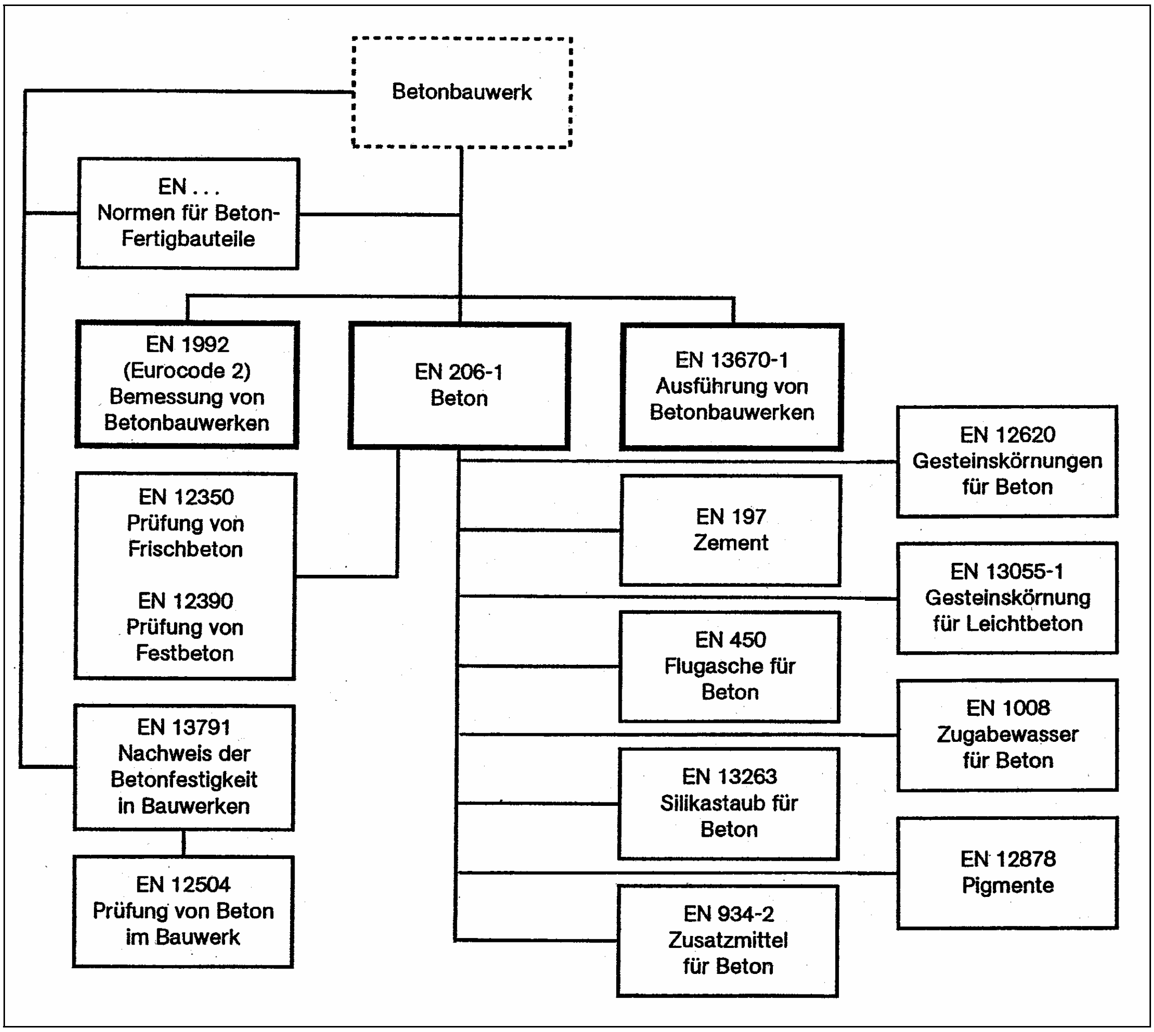

Figure 43: Relations between the EN 206-1 standard and other standards [DIN EN 206-1].

Based on the references to draft European standards in DIN EN 206-1 (not shown in figure 43), the DIN 1045-2 standard additionally lists German standards and regulations.

Except for fly ash (s. section 5.2.5), the standards on concrete constituents do not contain any requirements regarding the co-incineration of waste or pollutant concentrations. The requirements made with respect to the chemical composition refer to those constituents that are of relevance to concrete production and concrete properties.

In addition to the standards mentioned above, about 250 standards concerning buildings made of concrete, pre-fabricated concrete components, concrete test procedures, etc., were reviewed within the framework of this study. These standards only contain references to DIN EN 206-1 or DIN EN 197-1 (section 5.2.1) or to (partly outdated) German standards.

5.2.5 DIN EN 450 and fly ashes

As far as the origin of fly ashes in concrete is concerned, various possibilities exist. These relations are illustrated by figure 44. Use of coal as regular fuel in cement production leads to the generation of ashes that mainly enter the cement clinker and, hence, concrete. Moreover, fly ashes are added to the cement production process at various points as a raw material and also applied for the production of concrete.

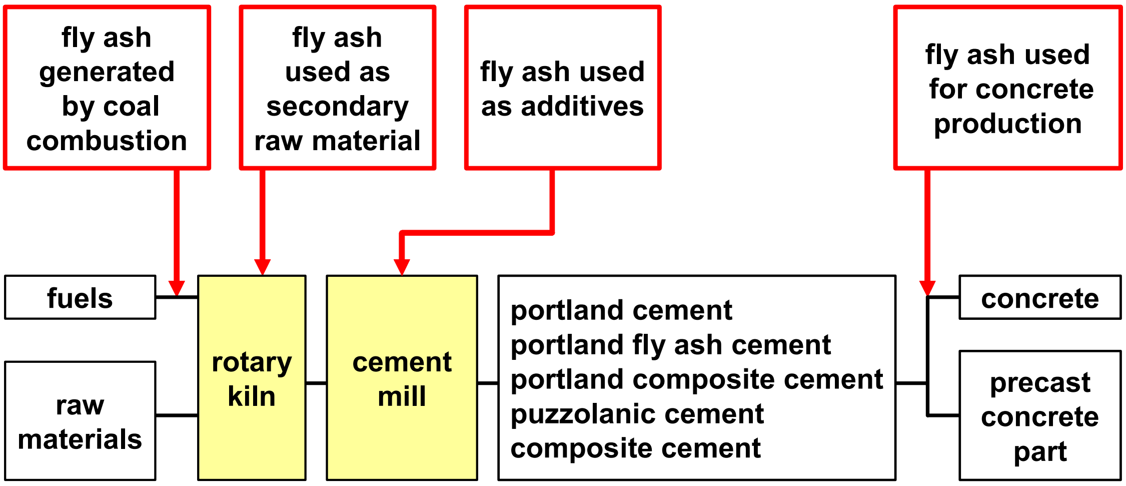

Figure 44: **Possible pathway of fly ash from power plants, similar to [Jacobs, 1982].**

Use of fly ashes in concrete production is governed among others by the DIN EN 450 standard. However, this standard does not apply to fly ashes used in the production of cement according to the DIN EN 197-1 standard.

According to the DIN EN 450 standard, fly ashes for the production of concrete must originate from furnaces operated with finely ground coal. As a consequence, fly ashes from power plants using sewage sludge or other secondary fuels may not be applied for the production of concrete. With respect to concrete properties, the standard among others contains requirements concerning the calcium oxide content, silicon dioxide content, and certain physical properties. Furthermore, the sulphate trioxide, alkali, and chloride concentrations are limited.

In addition to the DIN EN 450 standard, the requirements made in the Construction Products Lists (s. section 5.1.4) have to be taken into consideration. The Construction Products List A, part 1, annex 1.6 limit the validity of the standard to fly ashes generated when using certain types of coal. Moreover, up to 5 mass percent (dry matter) of sewage sludge, relative to dry hard coal, may be co-incinerated in German power plants.

For co-incineration the phosphorus content of sewage sludge, determined as P_2O_5 and related to the ash content of the sewage sludge, must not exceed 25 mass percent. In addition, the limit values listed in table 37 have to be observed.

Table 37: Limit values for sewage sludge co-incinerated in coal-fired power plants, the fly ashes of which are used for concrete production [Construction Rule List A].

Pollutant	Limit value mg/kg dry substance
Lead	900
Cadmium	10
Chromium	900
Copper	800
Nickel	200
Mercury	8
Zinc	2500

At the moment, a European draft exists for an amendment of DIN EN 450. It will consist of two parts in the future [DIN ENV 450-1, DIN ENV 450-2]. In contrast to the old version, co-incineration of selected waste materials will be possible in the future. These materials are listed in table 38.

The co-incinerated fractions are limited by additional requirements. Among others, 90% of the total ash have to originate from the coal used [DIN ENV 450-1].

Table 38: Maximum permissible fractions for co-incineration [DIN ENV 450-1].

Co-incineration material	Maximum Percentage by dry mass of co-combustion material related to coal %
Vegetable material like wood chips, straw, olive shells and other vegetable fibres	20 %
Green wood and cultivated biomass	8 %
Bone meal	2 %
Municipal sewage sludge	3 %
Paper sludge	5 %
Petroleum coke	10 %
Virtually ash free liquid fuels and gaseous fuels	20 %*

* Maximum percentage by calorific value of co-combustion material related to coal

5.2.6 Future modifications of construction product standards

Analysis of the standards for cement and several selected standards for concrete has revealed that the technical standards existing in the building sector are currently being harmonised on the European level. In the future, German standards for construction products will increasingly be substituted by European standards. Among others, European standards are being prepared for footpath decking slabs, curbstones, and paving stones [SLG, 2001].

Another modification refers to requirements with respect to health and the environment, which are not contained in the currently valid standards. Uniform regulations do not yet exist on the European level [VDZ, Tätigkeitsbericht]. This situation will certainly change in the future. To define the requirements in a more detailed manner, the existing European standards are planned to be revised within the next five years.

5.2.7 Technical Regulations for hazardous materials

The Technical Regulations for hazardous materials are set up by the hazardous materials committee and describe requirements for the handling of hazardous materials. Hazardous materials are defined by Article 3a of the “Chemicals Act – ChemG” [ChemG]. Among others, they are explosive, harmful to health or hazardous to the environment.

In the Technical Regulations for hazardous materials 613 “Substitute Materials, Substitute Processes, and Limitations of Use of Chromium-containing Cements and Chromate-containing Cementitious Preparations” [TRGS 613, 2002], requirements are made with regard to the chromium content. Chromate-containing cements may contain up to 100 ppm of chromium (VI) compounds with a soluble fraction of about 20%. Chromate-depleted cements may possess a soluble chromium (VI) fraction of less than 2 ppm only.

According to the requirements outlined by the hazardous materials legislation, the employer in general has to check whether substitute materials that are less harmful to health are available. As a consequence, chromate-depleted cements have to be applied preferably. The origin of chromium (VI), either from the raw materials or the wastes, is not relevant to the Technical Regulations for hazardous materials 613.

Since the beginning of 2000, only chromate-depleted packed cement has been on offer in Germany [Puntke and Wassing, 2002].

5.2.8 Guideline Assessment of the effects of construction products on soil and groundwater

The German Institute for Construction Technology (DIBt) in Berlin has drawn up a data sheet for the "Guideline Assessment of the effects of construction products on soil and groundwater" [DIBt, 2000]. The data sheet focuses on a two-stage assessment concept to acquire potential contaminations of the groundwater and soil. In total, four cases of application are distinguished, with the installation relative to the groundwater level (above/in the range of the groundwater) and the type of construction (water-permeable/impermeable) being taken into consideration.

As obvious from the flow chart of this assessment concept in figure 45, not all stages and steps of the assessment have to be passed under certain circumstances.

In the first stage of the assessment concept, the constituents of the construction product are determined quantitatively. For compliance with the requirements in the first assessment stage, certain hazardous substances or constituents, the use of which is prohibited (e.g. Ordinance on the Prohibition of Chemicals), shall not be contained in the building product.

If wastes are used for the production of the building product, the "unmixed and undiluted" waste has to be assessed according to the DIBt data sheet. If mineral waste is used, the requirements made in the LAGA rules "Requirements for the Utilisation of Mineral Waste – Technical Rules" [LAGA, 1997] have to be observed. The eluate contents have to be in compliance with the Z2 reference values. For the pollutant concentrations in the solid, uniform upper limits will have to be specified when revising the LAGA rules in order to prevent a pollutant accumulation in the materials cycle [DIBt, 2000].

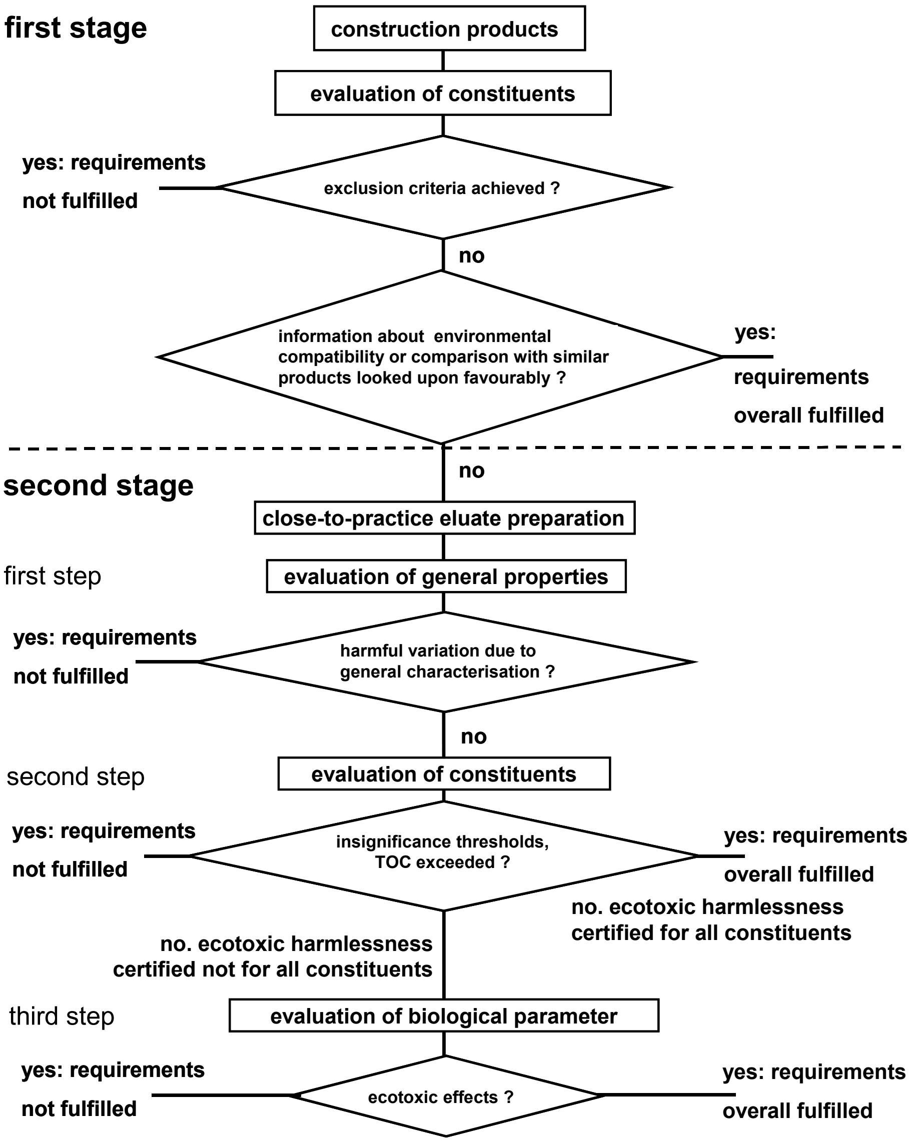

Figure 45: **Flow chart for the assessment of construction products with regard to soil and groundwater protection [DIBt, 2000].**

When using mineral waste for the manufacture of construction products, the first stage of the assessment concept requires the use of investigation methods that are only required by the second stage of the assessment concept when using other construction products without mineral waste (see below).

Under certain circumstances, i.e. when a construction product of identical composition has already been assessed according to the data sheet or environmental compatibility of all constituents has already been confirmed, the second stage of the assessment concept may be omitted.

The determination and evaluation of the mobilisable constituents of the construction product as envisaged in the second stage is based on a close-to-practice eluate preparation. The guideline only contains explanations for the selection of the elution process without requiring a standardised process in a binding manner. The second assessment stage is divided into three steps that do not always have to be executed. In the first step general properties, such as the pH value, electric conductivity, odour, colour, turbidity, and the eluate's tendency towards foam formation are assessed. In the second part of the data sheet, which is not yet available, construction product-specific limit values shall be given for the pH value and electric conductivity. Eluate investigation, the scope of which is specified as a function of the chemical composition, represents the second step. In this second step the results of the eluate investigation are to be assessed on the basis of insignificance thresholds that are given in table 39.

In connection with these insignificance thresholds, the measurement process to be applied is not indicated in the DIBt guideline. The Federal Ordinance on Soil Protection and Abandoned Contaminated Sites (BBodSchV) [BBodSchV] requires the DIN 38414-4 standard [DIN 38414-4].

The requirements given by the guideline for the second stage of the assessment concept are complied with when

- insignificance thresholds exist and are observed for all materials to be covered or when
- insignificant ecotoxic efficiency has been proved for all substances even without an insignificance threshold being indicated and the concentration of the total organically bound carbon (TOC) does not exceed 20 mg/l.

The third step of eluate investigation, including the fish test, algae test or other biological test methods, is only needed, if insignificance thresholds do not exist for all substances and insignificance of their ecotoxicological effects has not been proved.

To sum up, the concept for the assessment of construction products as given by the guideline is useful. If the requirements made in the guideline are observed, the respective building product is not supposed to cause any negative changes of the soil or groundwater contamination. If waste is used for the manufacture of the construction product, an assessment according to the guideline shall confirm harmless waste recycling.

Table 39: **Insignificance thresholds [DIBt, 2000].**

	Pollutant		insignificance thresholds *
Inorganic parameter	Antimony(Sb)	µg/l	10
	Arsenic (As)	µg/l	10
	Lead (Pb)	µg/l	25
	Cadmium (Cd)	µg/l	5
	Chromium, total (Cr)	µg/l	50
	Chromate (Cr)	µg/l	8
	Cobalt (Co)	µg/l	50
	Copper (Cu)	µg/l	50
	Molybdenum (Mo)	µg/l	50
	Nickel (Ni)	µg/l	50
	Mercury (Hg)	µg/l	1
	Selenium (Se)	µg/l	10
	Zinc (Zn)	µg/l	500
	Tin (Sn)	µg/l	40
	Cyanide , total	µg/l	50
	Cyanide, easy purgeable	µg/l	10
	Fluoride (F)	µg/l	750
Organic parameter	PAHs, total [1] naphthaline	µg/l µg/l	0.2 2
	Halogenated hydrocarbons, total [2]	µg/l	10
	Aldrine	µg/l	0.1
	DDT	µg/l	0.1
	PCB, total [3]	µg/l	0.05
	mineral oil hydrocarbons [4]	µg/l	200
	BTEX [5] Benzene	µg/l µg/l	20 1
	Phenols	µg/l	20

* Insignificance thresholds correspond to inspection values for assessment of the correlation soil-groundwater given in the soil protection and abandoned site ordinance.

1) PAHs, total: Sum of polycyclic aromatic hydrocarbons (PAHs) exclusive of naphthaline, methyl-naphthaline, as a rule determination of 15 substances according to the list of the Environmental

Protection Agency (EPA), exclusive of naphthaline, if necessary consideration of additional relevant PAHs (for example chinoline).

2) Halogenated hydrocarbons, total: Highly volatile halogenated hydrocarbons, sum of C1 and C2-hydrocarbons.
3) PCP, total: Sum of polychlorinated biphenyls, as a rule determination of 6 congeneres according Ballschmiter and AltölV(DIN 51527) multiplied by 5. substances, if necessary easy summation of all relevant substances (DIN 38407-3-2, -3-3).
4) n-alkane (C10 - C39) isoalkane, cycloalkane and aromatic hydrocarbon
5) BTEX: Highly volatile aromatic hydrocarbon (Benzene, toluene, xylene ethylbenezne, styrene, cumene).

However, some limit values and other regulations are still lacking in the current version of the guideline. They shall be included in the second part. This second part shall contain among others requirements with regard to the eluate process to be applied and product-specific limit values for general parameters (pH value and conductivity). In addition, it is envisaged to make more detailed requirements with regard to the compliance with insignificance thresholds.

In connection with the use of mineral waste, the guideline repeatedly refers to the LAGA rules "Requirements for the Utilisation of Mineral Waste – Technical Rules" [LAGA, 1997]. Due to the precisely defined scope of application by the use of the old five-digit waste code numbers, problems may be encountered when using the actual version in practice.

Furthermore, it must be taken into account that the approval of construction products will take place on the European level in the future. A standardised elution process that is to be applied on the European level for the production of a close-to-practice eluate is still lacking. So far, only draft requirements have been submitted.

Consequently, a final rating of the guideline cannot be made as long as the second part has not been adopted.

5.3 Waste legislation

In the Federal Republic of Germany, waste management activities and the handling of wastes are subject to the Waste Management and Recycling Act [KrW-/AbfG] that is concretised by a number of ordinances. The principles and basic obligations in the field of waste management and recycling are defined by articles 4 and 5 of the Waste Management and Recycling Act, where the hierarchy of avoiding, recycling, and disposal of wastes is outlined.

The definition of the term of waste as given in Art. 3, Par. 1 in combination with Annex I of the Waste Management and Recycling Act seems to be logical at first glance. In practice, however, it is not easy to separate between the waste and the product. Additional difficulties result from the inexact definition of the terms of “recycling” and “disposal”. The difference between recycling or heat recovery and disposal according to Art. 4, Pars. 3 and 4, only results from the requirement that the main purpose shall be the use of waste rather than the elimination of the pollution potential.

According to the Waste Management and Recycling Act, priority shall be given to heat recovery or materials recycling. According to Art. 6, Par. 1, Clause 2, the “type of utilisation that is more compatible with the environment” shall have precedence. By adopting legal ordinances, recycling or energy recovery may be requested for certain types of waste. In the past, however, the legislator did not made use of this option.

Only in Art. 6, Par. 2 does the Waste Management and Recycling Act contain precise requirements (calorific value of more than 11 MJ/kg and others) which have to be met at least by energy recovery according to Art. 4, Par. 4. But also this precise specification of the “limit value” of 11 MJ/kg is not undisputed in practice, as the “place of designation” is not indicated. An example is sewage sludge. In the mechanically dehydrated state (non-digested, dry matter content 35%), it has a calorific value of about 3 MJ/kg. In the thermally dried state (95% dry matter) it may well exceed calorific values of 12 MJ/kg [Gerhardt, 1999].

Apart from the requirements made in Art. 6, Par. 2 of the Waste Management and Recycling Act, no further information on the co-incineration of waste as a method of recovering heat from secondary fuels is given. This problem has been known for years, but an exact directive by the legislator, which is requested by industry time and again, is still lacking.

Moreover, recycling according to the Waste Management and Recycling Act has to be “proper” and “harmless”. Recycling is “proper”, if it is in compliance with the Waste Management and Recycling Act and other public regulations. This includes ordinances and administrative regulations under the Waste Management and Recycling Act as well as the Federal Immission Control Act, the Water Resources Management Act or other laws. The conception of proper recycling refers to the processes used for waste recycling, which among others are subject to the laws mentioned. In particular, the Federal Immission Control Act with its requirements regarding emissions has to be observed.

A “harmless” recycling takes place when public welfare is not affected and no pollutants are enriched in the materials cycle (Art. 5, Par. 3 Waste Management and Recycling Act). Other more precise requirements, for example, an investigation of the product “containing” the waste, are not envisaged by the Waste Management and Recycling Act. Consequently, it is not possible to distinguish reliably between “harmless” and “not harmless” recycling according to the Waste Management and Recycling Act (KrW-/AbfG).

Due to the “Ordinance on the Environmentally Compatible Disposal of Municipal Waste (Waste Disposal Ordinance – AbfAblV)” [AbfAblV], it may be assumed that volume flows of municipal wastes will change in the future. The ordinance allows for a legal operation of mechanical-biological waste treatment plants (MBA). Mechanical-biological treatment of domestic waste leads to a high-calorific fraction, for which a disposal path has to be found. Here, co-incineration in cement plants, in iron and steel industry or in power plants may be suited [Lahl and Zeschmar-Lahl, 2001].

Moreover, the federal government has adopted new ordinances related to the disposal of certain waste fractions. Apart from the Industrial Waste Ordinance and the Old Wood Ordinance, a new regulation has been adopted with respect to the disposal of waste oil. Potential consequences of these ordinances cannot yet be estimated.

Further changes may result from recent judgements of the European Court of Justice (C-228/00 and C-458/00). According to these judgements, waste utilisation in cement plants will increase, whereas waste incineration in waste incineration plants is classified to be a disposal measure. Waste-related criteria, such as the calorific value or pollutant contents, may not be used to distinguish between recycling and disposal. In principle, these judgements only refer to waste exports, but the waste management and legal consequences are being examined at the moment [NN, 2003].

5.3.1 RAL quality label “secondary fuels”

Since July 1, 2001, the RAL quality label “RAL-GZ 724 – Quality and Test Regulations for Secondary Fuels” developed by the Bundesgütegemeinschaft Sekundärbrennstoffe e.V. (BGS, Federal Association for the Quality of Secondary Fuels) has been acknowledged by the “RAL Deutsches Institut für Gütesicherung und Kennzeichnung e.V.” (RAL German Institute for Quality Assurance and Labelling). By means of this quality label, quality of secondary fuels applied in power plants or cement plants shall be ensured.

Secondary fuels subject to RAL-GZ 724 are produced from high-calorific wastes or fractions from households, trade, and industry. The quality and test regulations for the production of the respective secondary fuels contain precise requirements with regard to their production:

- Waste code numbers that are potentially envisaged for secondary fuel production (not requiring special supervision)
- Test regulations for first tests, own control , external control, and recurrent testing
- Sampling, scope of sampling, and scope of analytical investigation.

Moreover, the quality and test regulations comprise requirements with respect to the heavy metal contents to be observed. They are listed in table 40.

Table 40: Permissible heavy metal contents [BGS, 2001].

Pollutant	related to dry substance	heavy metal concentration (4) (Median)	heavy metal concentration(4) (80. percentile)
Cadmium (Cd)	mg/kg	4	9
Mercury (Hg)	mg/kg	0.6	1.2
Thallium (Tl)	mg/kg	1	2
Arsenic (As)	mg/kg	5	13
Cobalt (Co)	mg/kg	6	12
Nickel (Ni)	mg/kg	25 (1) 80 (2)	50 (1) 160 (2)
Selenium (Se)	mg/kg	3	5
Tellurium (Te)	mg/kg	3	5
Antimony (Sb)	mg/kg	25	60
Lead (Pb)	mg/kg	70 (1) 190 (2)	200 (1) - (3)
Chromium (Cr)	mg/kg	40 (1) 125 (2)	120 (1) 250 (2)
Copper (Cu)	mg/kg	120 (1) 350 (2)	- (3) - (3)
Manganese (Mn)	mg/kg	50 (1) 150 (2)	100 (1) 500 (2)
Vanadium (Vn)	mg/kg	10	25
Tin (Zn)	mg/kg	30	70
Beryllium (Be)	mg/kg	0.5	2

(1) Secondary fuels being made of waste from industry

(2) Secondary fuel generated from municipal waste fractions with high calorific value

(3) Specification requires information about secondary fuel conditioning, specification will be carried out later.

(4) Heavy metal concentrations are valid for heating values ≥ 16 MJ/kg for municipal waste fractions with high calorific value and for waste from industry with a heating values ≥ 20 MJ/kg . The values have to be linearly decreased for lower heating values. Increasing is not possible.

The RAL quality label does not apply to liquid wastes and fuel from old wood [BGS, 2001]. For further details, it is referred to the quality and test regulations of the BGS [BGS, 2001] and other literature [Flamme and Gallenkemper, 2001].

The first RAL-GZ 724 quality label was granted to a processing and conditioning plant in Erftstadt (Germany). For another three plants, the acknowledgement procedure is under way [Euwid, 2002a], [Karnick and Glorius, 2002].

5.3.2 RAL quality label “recycling products from used wood”

The Gütegemeinschaft Gebrauchtholz-Recyling e.V. (Association for the Quality of Used Wood Recycling) in cooperation with research institutes, industry, and experts has developed an RAL quality assurance system (s. section 5.3.1) for the recycling of (RAL-GZ 428/1) and energy recovery (RAL-GZ 428/2) from the recycling products of used wood. This quality assurance system is outlined in the respective RAL quality guideline [RAL, 2001] and currently being revised. By the addition of another five partial guidelines, processing products from solid biomass for energy recovery or recycling shall be certified in general in the future [RAL, 2001].

5.4 *Immission Control Legislation*

The Federal Immission Control Act [BImSchG] with the complementing ordinances represents the legal basis of measures taken for air pollution control and other provisions on environmental protection in the Federal Republic of Germany.

Article 5 of the Federal Immission Control Act is of general significance to the operation of technical facilities. Here, general requirements are outlined. When strictly interpreting Art. 5, Para. 1, No. 3 of the Federal Immission Control Act, the requirements made with respect to the avoiding or recycling of wastes are of relevance to cement quality. With regard to the operation of a cement plant, they mean that dusts removed from the production process have to be fed back into it. Taking into consideration Waste Management and Recycling Act, a removal and subsequent disposal of dusts loaded with trace elements should be impossible.

The Federal Immission Control Act does not contain any precise licensing requirements with respect to plant operation or emission limits. The emission limits and other requirements are given in the corresponding ordinances, administrative regulations, and technical regulations.

Incineration of waste is subject to the Ordinance on Incineration Plants for Wastes and Similar Burnable Substances [17. BImSchV]. This ordinance applies to waste incineration plants as well as to the co-incineration of waste in industrial facilities, such as power plants or cement production plants.

In the past, co-incineration of waste was repeatedly discussed due to the so-called mixing rule that is provided for by the Ordinance on Incineration Plants for Wastes and Similar Burnable Substances. The mixing rule is used to calculate the emission limits on a pro rata basis from the resulting flue gas volume flows of regular fuels and wastes in case of a co-incineration of waste in industry plants. In this connection, it must be noticed that the emission limits for waste incineration, which are also given by the Ordinance on Incineration Plants for Wastes and Similar Burnable Substances, usually are far smaller than the requirements made for the use of regular fuel. The emission limits for cement production plants using regular fuel are specified by the Technical Instructions on Air Quality Control [TA Luft]. The changed requirements of the Technical Instructions on Air Quality Control due to an updating of the regulations in 2002 are illustrated by table 41.

Table 41: Emission limits according to the Technical Instructions on Air Quality Control (TA Luft) (selection) [Hoenig, 2002], [TA Luft].

Pollutant		**TA Luft 1986**	**TA Luft 2002**
NO_x (as NO_2)	g/m³	0.80 / 0.50	0.50
SO_2	g/m³	0.40	0.35
HCl	mg/m³	30	30
HF	mg/m³	5	3 (gaseous inorganic substances Kl. 2)
PCDD / F	ng/TE/m³	- (command for minimisation)	0.1
Benzene	mg/m³	5	5 (target value 1)
Dust	mg/m³	50	20

Without explaining details, it must be underlined that the Ordinance on Incineration Plants for Wastes and Similar Burnable Substances contains requirements that are not contained in the Technical Instructions on Air Quality Control and vice versa.

Mixing calculation as a means to determine emission limits for the co-incineration of waste seems to be logical. In practice, however, difficulties are encountered for various reasons.

Detailed information on the problems associated with the calculation of emission limits and the previous licensing practice for the co-incineration of waste may be obtained from literature [Blümel and Nagel, 1996], [LAI], [Lübbe-Wolf, 1999], [PROGNOS-Gutachten].

Due to the adoption of a new “Directive 2000/76 of the European Parliament and Council on the Incineration of Waste” dated December 4, 2000, [RL 2000/76] by the European Union (EU), the procedure of determining emission limits for the co-incineration of waste in cement plants will change. Contrary to the previous practice of mixing calculation, specific limit values are given for the co-incineration of waste in cement plants in annex II.1 of the directive 2000/76.

The amended Ordinance on Incineration Plants for Wastes and Similar Burnable Substances that will be required as a consequence of the newly adopted EU directive had not yet been submitted as a legally binding version when the project work was completed. The following statements refer to the draft modified ordinance [17. BImSchV 2002] and additional information (among others [Euwid, 2003], [Gleis, 2003]).

Accordingly, the amended version of the Ordinance on Incineration Plants for Wastes and Similar Burnable Substances will take over the existing limit values for waste incineration and complement them by an additional integral parameter covering arsenic, benzopyrene, and other carcinogenic substances (s.a. table 42). The new version of the Ordinance on Incineration Plants for Wastes and Similar Burnable Substances gives fixed emission limits for the co-incineration of waste in cement plants, which in some cases are stricter than the values given by the EU directive 2000/76. The future emission limits are listed in table 42.
The competent authority may allow higher limits for some pollutants, provided that the higher emissions are caused by the raw materials.

From a share of more than 60 % in the incineration heat output, emission limits required waste incineration are generally requested for cement plants. In this case, it is possible to specify mixed limit values for NO_x and dust at request. With a few exceptions that are not mentioned here, the waste incineration requirements have to be met, if the share of waste requiring special supervision exceeds 40 %.

Table 42: Emission limits of the amended 17. BImSchV for the use of waste in cement plants (up to 60 % of incineration heat output).

Pollutant	Emissions limit (10 Vol.-% O_2)		
Dust	*	20	mg / Nm^3
HCl	*	10	mg / Nm^3
HF	*	1	mg / Nm^3
NO / NO_2 as NO_2	*	500	mg / Nm^3
SO_2 / SO_3 as SO_2	*	50	mg / Nm^3
Carbon	*	10	mg / Nm^3
Hg	*	0.03	mg / Nm^3
CO	*	50	mg / Nm^3
PCDD and PCDF	**	0.1	ng / Nm^3
Cd, Tl	**	0.05	mg / Nm^3
∑ Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn	**	0.5	mg / Nm^3
∑ As, Benzo(a)pyren, Cd, Co, Cr	**	0.05	mg / Nm^3

* daily average value, half-hourly average values not listed

** average value measured over sampling time

5.4.1 VDI regulation 2094

The VDI Regulation 2094 “Emission Control Cement Plants” [VDI 2094, 2003] first was available in the draft version of March 2001 only. The final version was published in March 2003. This regulation describes the cement production techniques as well as emission control measures or measures for the control of individual pollutants.

In addition, section 4 of the VDI Regulation 2094 entitled “Use of wastes in the Cement Industry” deals with the utilisation of waste in cement industry. As far as the impacts on product quality are concerned, it is underlined that concentrations of individual elements may both increase or decrease by the use of waste. The mobilisation of trace elements from concrete and mortar is considered to be “small” without any data being given. According to the regulation, extensive investigations confirm a tight incorporation of trace elements in the cement matrix. However, only a few literature sources are given to support this statement.

For the selection of secondary fuels and criteria to assess wastes, it is only referred to the LAGA paper “Criteria for Energy Recovery from Waste” [LAGA, 1997]. This paper is available in the draft version only and has not yet been adopted.

Limits for pollutant contents of the waste materials are not given by the regulation. For some statements with respect to the use of waste in cement industry and in particular the incorporation of pollutants in cement, a more precise explanation would have been useful.

6 Summary and Conclusion

This project was aimed at investigating the impact of the use of secondary fuels, secondary raw materials, and interground additives on trace element concentrations in cement and concrete. Furthermore, it was to be investigated under which conditions and to which extent the incorporated trace elements may be released into the environment. Additionally, it was to be found out whether regulations, standards, directives, etc. for the production of cement and the corresponding construction products contained specific requirements in terms of pollutant loads.

The study has shown that presently used secondary input materials in some cases result in a slight increase in trace element concentrations of cement. However, a general assessment of the use of wastes in cement production and of its impact on trace element input cannot be made. Furthermore, future developments can hardly be estimated.

The mobilisation of trace elements from concrete components during service life is negligibly small. After demolition, an increased trace element mobilisation is conceivable under certain assumptions. However, the present knowledge is not sufficient for a final judgement to be made.

Existing regulations regarding the production and use of cement do not yet contain any requirements in terms of permissible concentrations of pollutants. However, changes can be expected in future due to requirements that are presently being conceived on the European level.

To investigate the contribution of secondary fuels, secondary raw materials, and interground additives to total trace element concentrations in cement and concrete, **model calculations for material flows** within the system were performed using different calculation approaches. It may be assumed that model calculations reproduce the effect of the use of secondary fuels on the total trace element concentration of cement far better than the corresponding measurements. Measurements only represent snapshots and depend on a number of influencing factors. For instance, an increased trace element concentration in a selected input material inevitably leads to higher concentrations of trace elements in cement on the average, even if measurements do not show this effect, as it is superposed by varying trace element concentrations of other input materials. Only when secondary materials exhibit far higher trace element concentrations than primary materials will much higher trace element concentrations be measured in cement.

The extensive database used for the model calculations is based on approximately 300 data sources. The average values calculated for the trace element concentrations of raw meal components and regular fuels lie in the upper range of the values published by the VDZ. For some elements they even exceed the maximum values given in the VDZ publication. Thus, the calculated contribution by raw meal and regular fuels to total trace element concentrations in cement may possibly be overestimated, while the contribution by other input materials, such as secondary fuels, may be underestimated.

Input materials from iron and steel industry are characterised by a strong heterogeneity and a large range of trace element concentrations. Since it may be assumed that materials (especially dusts) with high trace element concentrations are not used for the production of cement, average minimum values derived from the minimum values given in literature were used for model calculations instead of average values. For the calculation of these average minimum values highly loaded dusts, ores, etc. were not taken into consideration, since it may be assumed that these materials are not used as input materials in the production of cement.

The following results are obtained from the analyses:

1. **There is a good agreement between the calculated trace element concentration values for normal cements and the corresponding VDZ measurements.**
2. **Secondary input materials contribute to the total trace element concentration of cement. Although primary raw materials represent the most important input pathway, they cannot be considered the only relevant source of trace element concentration in cement.**

   In addition to secondary fuels, secondary raw materials, especially substitute materials from iron and steel industry and coal fly ashes, play an important role. The share of each individual input material in the total trace element concentration of cement varies from trace element to trace element.

3. **The amount of wastes used as input materials in 2001 was higher than in 1999. According to calculations, trace element concentrations of the cements are slightly higher for 2001 than for 1999. For cadmium, antimony, thallium, and zinc the increase amounts to up to 12%.**

   For all other elements taken into consideration the increase is a few percent only and, hence, lies in the range of the 1999 trace element concentrations calculated for cement. Contrary to 1999, large amounts of meat and bone meal were used as secondary fuel in 2001. Compared to other secondary fuels, the trace element concentration of meat and bone meal is relatively low. If other secondary fuels, such as fractions of industrial, commercial, and municipal wastes, used tyres, sewage sludge, etc. would have been used instead of meat and bone meal, the increase of trace element concentration in cement would have been even higher.

4. **The use of waste in cement production has an impact on the trace element concentration of cement. An increase of the trace element concentration of cement due to the use of waste as input material was found for antimony, cadmium, and zinc, as revealed by calculations for different scenarios.**

   Using waste as input material, the concentration values of these elements in cement exceed the upper range of the trace element concentrations resulting when producing cement without using any waste as input material. Also lead and cobalt concentrations increase when using waste as input material, but this increase is less pronounced. For all other elements there are no significant effects resulting from the use of wastes. Increased antimony and zinc concentrations of cement result from the use of secondary fuels. In the case of cobalt, lead, and cadmium, secondary raw materials and interground additives are responsible for the slight increase of the trace element input into cement.

5. **Trace element concentrations of concrete result from the input materials cement, coal fly ash, and basalt and slag aggregates.**

   In the scenarios studied a reduction of trace element concentrations in concrete, especially of copper, nickel, lead, arsenic, and zinc, can be achieved soonest by doing without coal fly ash as an additive. However, the environmental impact is not only influenced by the total trace element concentration in concrete, but especially from the fraction that is potentially mobilisable. Under physical aspects, trace elements incorporated in materials with a high surface to volume ratio (potentially higher dissolution kinetics) may be classified as potentially mobilisable in the long run. As a consequence, it cannot be excluded that trace elements from materials like cement and coal fly ash, can be mobilised in the long term.

6. **All trace elements which enter cement from different sources are incorporated in hardened cement paste in the medium term.**

   This also applies to trace element loads from coal fly ash, irrespective of whether it is used as a raw meal substitute in cement production, as a main or minor constituent of cement or as concrete additive.

7. **For the use of chlorine-containing secondary materials gas bypasses are increasingly installed in cement plants so as to relieve the chlorine circuits.**

   Eventually, the produced bypass dust is co-ground with the cement. This measure allows to use new secondary materials of high chloride content at least temporarily for cement production, since the extra chloride can be dispersed in the product over a long period of time. On the other hand, the permissible chloride content in the cement product can be made use of to a large extent. In this way, higher quantities of chloride-rich secondary materials can be applied. In the future, the mean chloride content of all produced cements may increase to the maximum permissible value. Since potential changes of the trace element loads, which may be associated with an increased use of chloride-rich secondary materials, are not known, future development of the trace element contents of cement can hardly be estimated. If required, the chlorine bypass dusts as a small material flow could be discharged as a reduction measure.

8. **A few hours after concrete mixing already are the trace elements almost quantitatively fixed in the highly alkaline cement paste. The cement paste is buffered strongly in the pH range of 12-12.5. As long as the buffer remains effective, it forms a stable sink for trace elements. This generally holds over the entire service life.**

9. **After service life, concrete and mortars are crushed by demolition and processing. Due to the enlarged surface area, crushed concrete weathering is accelerated under normal conditions. In order to avoid an environmental risk caused by the trace elements, the type of utilisation is of decisive importance.**

   If the surface area of concrete is strongly enlarged, the buffering effect of the hardened cement paste collapses. The primarily formed hydrate phases are slowly converted, thus changing the mobility of the trace elements. The underlying reactions are only partly known and not simulated by traditional test procedures. To avoid potential mobilisation mechanisms, crushed concrete should be reused in a spatially concentrated manner in order to maintain the high buffering potential of the cement paste as long as possible. In the ideal case, crushed concrete should be used as concrete aggregate and not in unbound road construction. The influence of biota on weathering after service life is unknown to a large extent.

10. **The long-term behaviour of trace elements in crushed concrete could not be predicted reliably under this project due to the still insufficient scientific knowledge.**

    It is not yet clear whether trace elements are increasingly mobilised after service life. The factors (reactive surfaces, pH of surface water, thermodynamic stability of the cement hydrates and of their weathering products, kinetics of reactions, etc.) influencing the performance are extremely complex. Reliable predictions may only be obtained by the combined modelling of the weathering scenario, the geochemical behaviour of the cement hydrates, and the physical properties of the concrete. Also in the near future, such predictions will hardly be possible due to the enormous amount of research required for an improved geochemical modelling. However, work that has already been performed on the geochemical modelling of the long-term behaviour of hardened cement paste in nuclear repositories may be made use of.

11. **So far, standards and regulations for the production of cement and corresponding construction products do not contain any special requirements as regards permissible pollutant concentrations.**

    Existing guidelines only refer to the hydraulic behaviour of cement. Due to activities on the European level, however, changes regarding permissible trace element concentrations of cement may be expected in the future.

12. **While the use of fly ash from power plants as an input material in the production of cement is not subject to any regulations, implicit requirements exist for trace element concentrations of fly ashes used as an additive in concrete production.**

13. **Following a first evaluation of two recent judgements of the European Court of Justice (C-228/00 and C-458/00) by organisations, industrial representatives, etc., it may well be expected that these judgements will influence the waste flows. The use of waste in cement industry may be expected to increase in the future.**

7 Excursus: emission and transfer factors

7.1 *Survey*

In clinker production trace elements enter the process via raw materials and fuels and leave it together with the clinker or cement or by emission into the atmosphere. In raw materials the trace elements are bound in a mineral matrix and heated up to 1450°C – 1500°C in the heat exchanger/rotary kiln system. In fuels trace elements are mainly bound in an organic matrix. It completely enters the gas phase at temperatures of up to 2000°C except for the low-volatile inorganic fraction [Fehringer et al., 1999, (PRIZMA-Studie)]. For this reason, probability of a substance entering the gas phase in the heat exchanger/rotary kiln system is supposed to be higher for fuel-borne substances than for raw material-borne substances. The substances existing in the gas phase condense largely as a function of temperature on the counterflowing raw meal particles and the fine dust. Part of the fine dust may leave the heat exchanger/rotary kiln system together with the offgas flow.

To determine the emissions resulting from the fuel, two different approaches are applied. The so-called **black-box method** serves to determine so-called emission factors. The other approach consists in calculating the emission based on the **rate of incorporation in the heat exchanger/rotary kiln system and the separation efficiency of the electrostatic precipitator.** From this, the transfer factors are determined. In addition, formulas to determine emission and transfer factors were derived by the VDZ based on a model-like description of a two-stage system (heat exchanger/rotary kiln and electrostatic precipitator). These approaches and the assumptions associated with them shall be dealt with in more detail below.

7.2 *Black-box method*

Using this method, only the flows entering (input flows) and leaving the system (output flows) are considered. Processes taking place inside the system are not covered by the calculation. Accordingly, the emission factor results from the ratio between total emission and total input.

$$\mathrm{EF} = \frac{\mathrm{S_E}}{\mathrm{S_B} + \mathrm{S_R}}$$

where

EF	=	emission factor	S_E	=	substance load emitted
S_B	=	substance load of the fuel	S_R	=	substance load of the raw material

This approach is based on the assumption that the behaviour of trace elements contained in the raw materials is identical with the behaviour of trace elements from fuels. An increase in the trace element input would lead to a proportional increase in emission, irrespective of whether the input is increased in fuels or raw materials.

In this connection, it is pointed out by the “Arbeitshilfe Stoffflussanalyse bei abfallrechtlichen Beurteilungsfragen” (Material Flow Analysis as an Aid in Assessment under Waste Management Legislation) of the Ministry of the Environment and Nature Protection, Agriculture, and Consumer Protection of the state of Northrhine-Westfalia [MURL, 2001]:

“This approach represents a simple model study and yields maximum values, as no variation of incorporation is considered for substances from raw materials and from fuels.”

If incorporation of trace elements from fuel is smaller than incorporation of trace elements from raw materials, however, this approach does not necessarily yield maximum values for the emission factors.

7.3 Incorporation rate times separation efficiency method

This approach allows for a determination of emissions originating from the fuel. The transfer factor is obtained according to the following formula:

$$TK = (1 - \gamma) \cdot (1 - \eta) \cdot \varepsilon$$

where

TK = transfer factor

γ = incorporation rate of fuel-borne substances in the heat exchanger/rotary kiln system

η = dust separation efficiency

ε = ratio between the concentration in the clean gas fine dust to the concentration in the offgas fine dust

At the moment, however, hardly any data are available for γ and η, which allow a distinction to be made between fuel and raw material. Consequently, the values calculated with this approach have to be considered a rough approximation only. In this respect, it is pointed out by the PRIZMA study:

“Transfer factors of substances that enter the system together with the fuel cannot be calculated exactly by means of balancing calculations, as the emissions from cement

production plants consist of material flows of raw materials and – to a varying extent – of material flows of fuels. At the moment, these material flows cannot be distinguished."

In spite of these reservations, transfer factors are calculated and tabulated for individual plants in the PRIZMA study.

7.4 Derivation of emission and transfer factors by modelling a two-stage system (VDZ)

Figure 46 shows the two-stage system used for the determination of emission factors. Figure 47 shows the two-stage system used to derive transfer factors for fuel-borne trace elements. Both representations were taken over from the VDZ. The first stage represents the electrostatic precipitator of separation efficiency η_1, the second stage the heat exchanger/rotary kiln system of separation efficiency η_2. E_η describes the input via the fuel, $E_{1-\eta}$ the input via the raw material, A_η the output via clinker, and $A_{1-\eta}$ the output via emission.

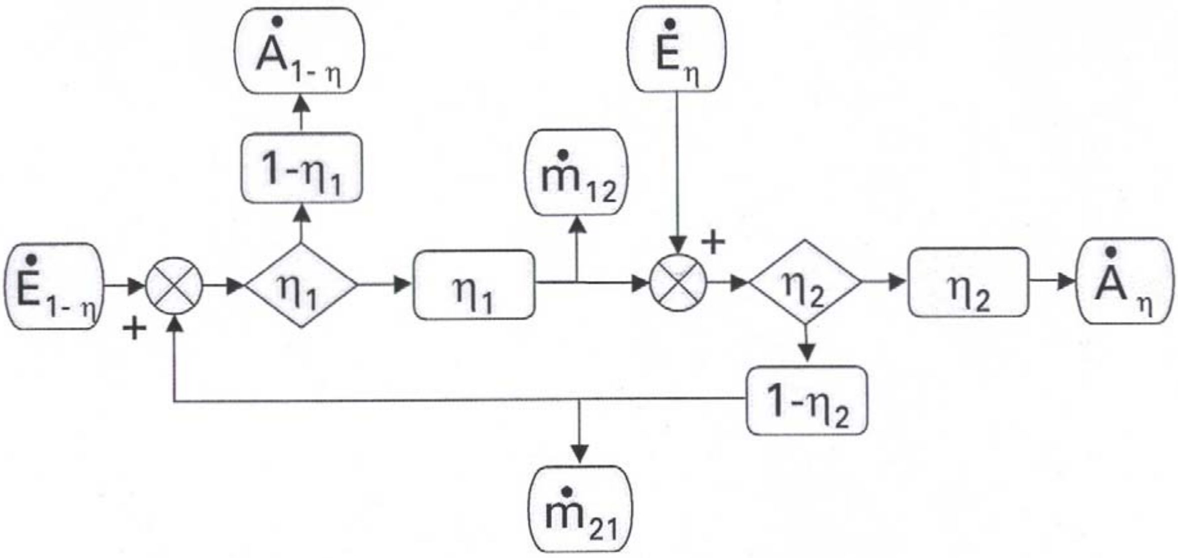

Figure 46: Two-stage model system used for the derivation of emission factors [Locher, 1999].

It is crucial to the system and, hence, the determination of transfer factors that the fuel E_η first has to pass the heat exchanger/rotary kiln system before the trace elements that are not discharged together with the clinker enter the electrostatic precipitator with the trace elements contained in the raw material $E_{1-\eta}$. As a consequence, the fuel experiences an additional resistance. With the same separation efficiency η_2 of the heat exchanger/rotary kiln system, probability of entering emission is far smaller for the fuel than for the raw material.

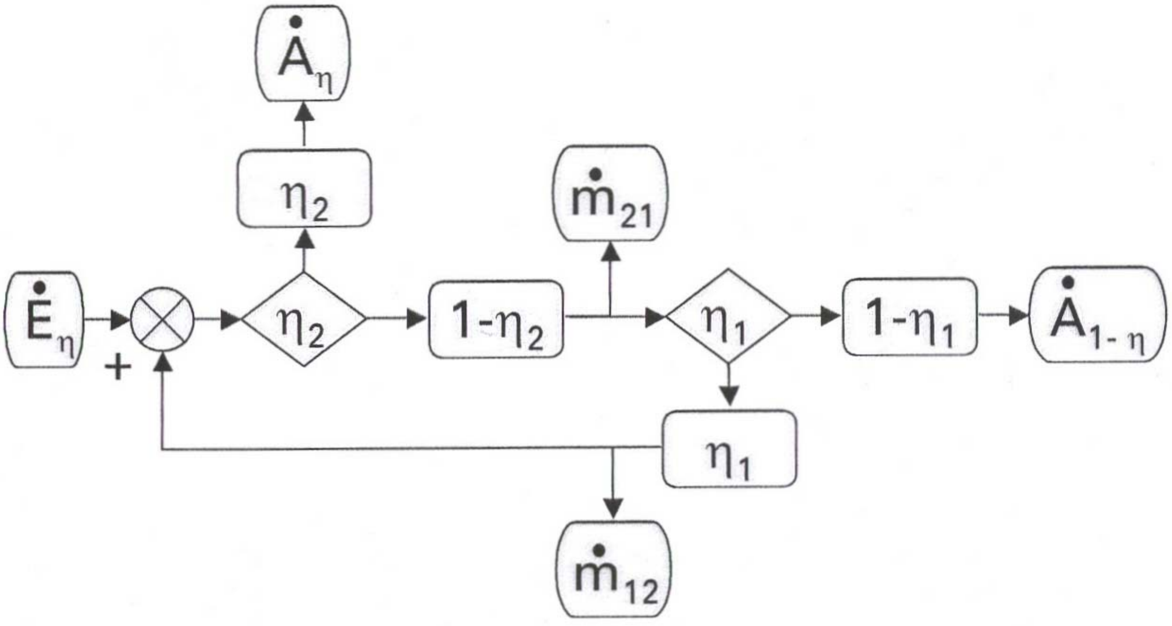

Figure 47: **Two-stage model system used for the derivation of transfer factors [Locher, 1999].**

Calculations lead to the following emission factor

$$EF = \frac{1-\eta_1}{E_\eta + E_{1-\eta}} \cdot \frac{E_{1-\eta} + E_\eta \cdot (1-\eta_2)}{1-\eta_1 \cdot (1-\eta_2)}$$

and to the following transfer factor for fuel-borne substances

$$TK = \frac{(1-\eta_1)\cdot(1-\eta_2)}{1-\eta_1 \cdot (1-\eta_2)}$$

This approach is based on the assumption that η_1 and η_2 are identical for fuel-borne substances and raw material-borne substances, which is not necessarily the case. As the fuel in the heat exchanger/rotary kiln system experiences an additional resistance, the transfer factor of fuel-borne substances is far smaller than the emission factor representing the ratio between total emission and total input.

Analysis of the emission factor equation also yields the following results:

For given η_1 and η_2 and a fixed value of the trace element concentration in the raw material, an increase in the trace element concentration of the fuel leads to a decrease of the emission factor, as the total input, the value of which is given in the denominator, increases more strongly than emission, the fuel-borne fraction of which experiences an additional resistance in the heat exchanger/rotary kiln system, as was mentioned above.

Hence, the VDZ approach described is characterised by the following features:

- The emission factor depends on the distribution of the total trace element input over fuels and raw materials.
- Separation efficiencies in the heat exchanger/rotary kiln system (η_2) and the electrostatic precipitator (η_1) are identical for fuel-borne substances and raw material-borne substances, which is not necessarily the case in reality.
- Due to the additional resistance experienced by fuel-borne substances in the heat exchanger/rotary kiln system, the transfer factor of fuel-borne substances is far smaller than the emission factor.

7.5 Data on emission and transfer factors

In the PRIZMA study emission and transfer factors of the elements mercury, cadmium, lead, and zinc are calculated for a plant with a grate-type pre-heater and for four plants with a cyclone pre-heater.

To determine the emission factors, data on the average trace element concentration of the raw materials mixtures and fuels, the input of raw materials and fuels, and the emission of individual trace elements of the individual plants are used. These data are documented in the study mentioned.

To determine transfer factors, values for the incorporation rate, separation efficiency, and accumulation factor are given for the individual plants. These data are mainly taken from literature such that the values used may be considered plant-specific in exceptional cases only. Also these data are documented in the study mentioned.

Emission factors given by the VDZ are based on measurements in the individual plants. The transfer factors were calculated based on the model described above, with the separation efficiency values taken from literature.

Figures 48 to 50 show the emission and transfer factors determined for lead, mercury, and cadmium according to different sources. TK1 through TK 4 denote transfer factors for plants in Austria [Fehringer et al., 1999], EF1 through EF4 the respective emission factors. TK-VDZ represents the transfer factor calculated by the VDZ. EF-SFA is the emission factor used in material flow analyses in Northrhine-Westfalia. In addition, the emission factor EF-BZL is indicated. It represents the average value for cement plants in Northrhine-Westfalia and is based on data given by Winkler [MURL, 2001].

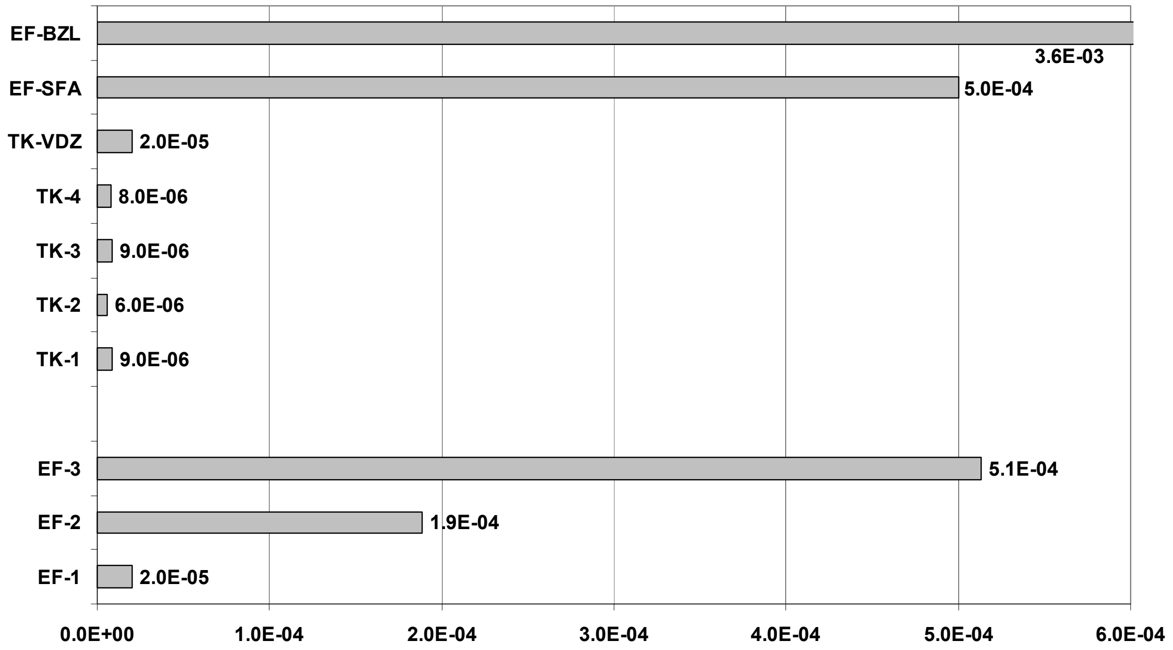

Figure 48: **Emission and transfer factors for lead according to [Fehringer et al., 1999], [MURL, 2001].**

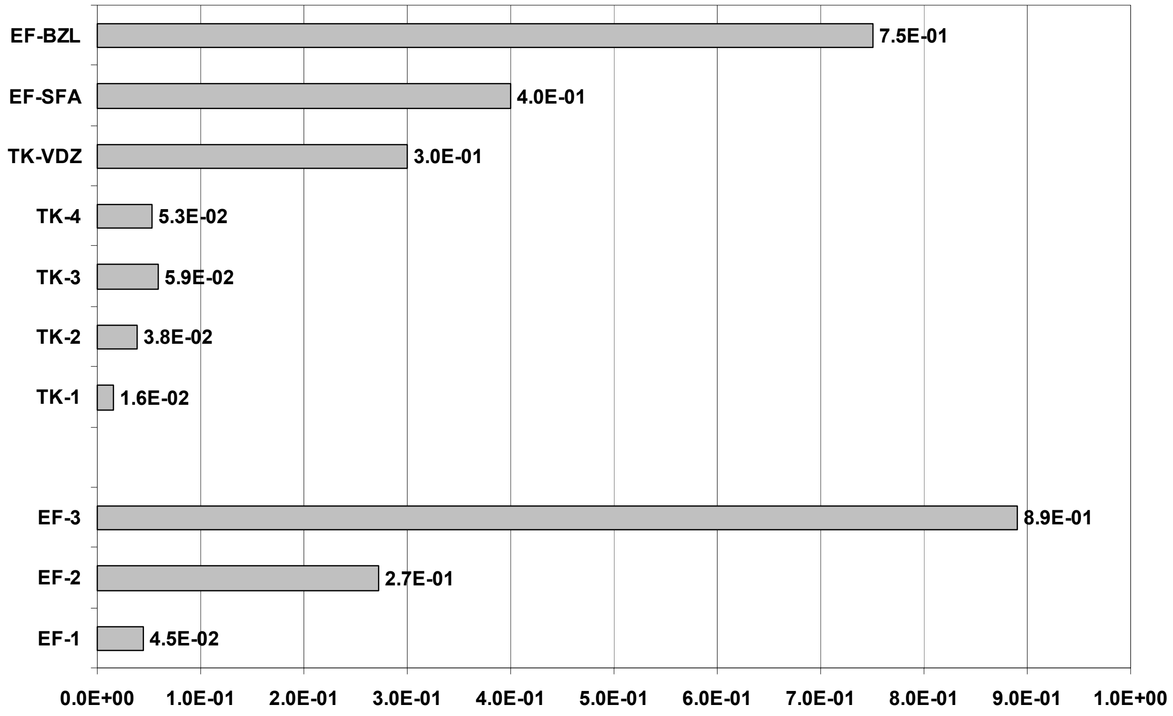

Figure 49: **Emission and transfer factors for mercury according to [Fehringer et al., 1999], [MURL, 2001].**

As a whole, it may be noticed that both the emission and transfer factors may differ by more than an order of magnitude depending on the plant and data source.

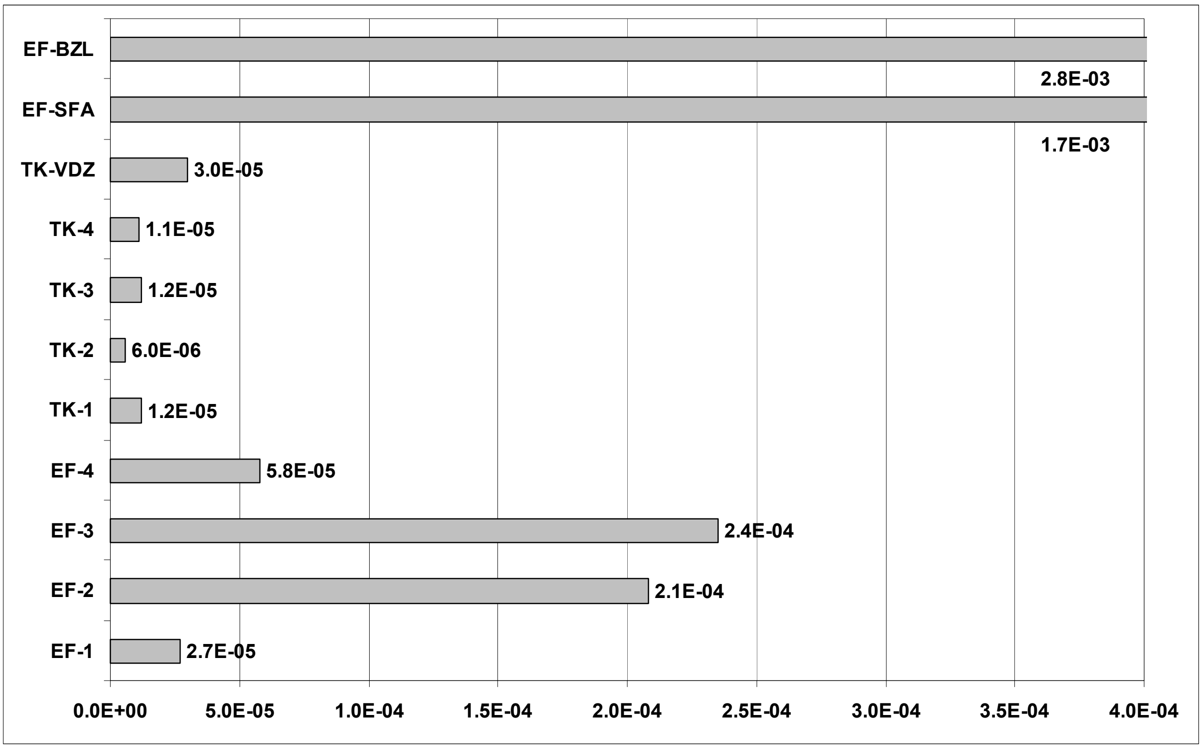

Figure 50: **Emission and transfer factors for cadmium according to various sources [Fehringer et al., 1999], [MURL, 2001].**

7.6 Evaluation of emission and transfer factors

As described in the previous sections, determination of emission factors is based on the assumption that raw materials and fuels exhibit an identical behaviour in the plant. Hence, a change of the trace element input leads to a proportional change of emission, irrespective of whether it takes place in the fuel or raw material. In case trace elements from the fuel possess a higher probability of entering emission than trace elements from the raw material, this approach possibly leads to an underestimation of the trace element emissions associated with the use of fuel. Consequently, the emission factor determined using the approach described above does not always represent a conservative estimation.

Lacking data on the trace element input of individual plants, the generally not existent correlation between the input quantity and the emission measured, and the complexity of the processes taking place in the plants for clinker production result in the fact that the emission factors given in literature partly differ by more than an order of magnitude. Also the use of e.g. annual mean values of trace element inputs via raw materials and fuels is not supposed to result in any improvement of the quality of emission factors. In this case, only mean emission factors are obtained, which are not even representative of the plant studied.

Transfer factors distinguish between trace elements from fuels and trace elements from raw materials. As the data required for this purpose are still lacking, data not making such a distinction have to be used. Hence, this approach also yields uncertain results with large variations. Due to the complex processes taking place in clinker production plants and the accordingly high expenditure required in terms of measurement methods, such data will hardly be available in the future.

Derivation of emission and transfer factors by modelling clinker production using a two-stage system is based on the assumption that trace elements from raw materials and fuels reach the same rate of incorporation in the electrostatic precipitator and the heat exchanger/rotary kiln system. Moreover, it is assumed that contrary to trace elements from raw materials, trace elements from fuels experience an additional resistance in the heat exchanger/rotary kiln system, as a result of which their probability of entering emission is much smaller. Also this approach is associated with the difficulty of using representative incorporation rates for the calculations.

If a certain type of waste is to be used in a cement plant, the question arises to the licensing authority, whether the use of this type of waste can be permitted. For this purpose, the "Arbeitshilfe Stoffflussanalyse bei abfallrechtlichen Beurteilungsfragen" (Material flow analysis as an Aid in Assessment under Waste Management Legislation) was developed. Among others, it is used in Northrhine-Westfalia. This aid also contains emission factors for cement plants. These values are based on values measured by the VDZ in the individual plants and were included in the aid after intensive discussions among various groups of interested parties (see figures 48 through 50, bar EF-SFA). These emission factors are used to check in advance whether certain emission limits associated with the use of waste are observed. Irrespective of this preliminary estimation, continuous measurements are to be carried out during actual use of these wastes in order to ensure that the given emission limits are observed. As no better method exists at the moment, this procedure seems to be reasonable. As described by the aid, however, plant-specific data should be used to the largest possible extent.

Due to lacking data and the resulting large variations of the emission and transfer factors, however, these data are not suited for material flow analyses and for obtaining reliable statements with regard to the distribution of trace elements over certain partial flows o the plant. For this reason, these values were not used for calculations made within the framework of the present study.

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9 Annex

Table A1: **Extent of data availability on different input materials being used for cement production and on intermediate and final products. + = good data availability, 0 = satisfying data availability, - = dissatisfying data availability.**

Primary raw materials	
Limestone	+
Marl	-
Clay	+
Sand	-

Secondary raw materials	
Iron ore	-
Foundry sand	-
Bottom ash	0
Coal fly ash	+
Materials from iron and steel works	0

Regular fuels	
Brown coal	0
Hard coal	+
Oil coke	-

Secondary fuels	
Scrap wood	0
Waste oil	-
Used tyres	-
BPG* / SBS*	+
Paper waste	+
Plastic wastes	+
Paper/plastic mixtures	0
Automobile textiles	0
Meat and animal meal	0

Intermediate and final products	
Raw meal	0
Clinker	+
Portland cement	0
Blastfurnace cement	-

Interground additives	
Gypsum/Anhydrite/FDG gypsum	0
Blast-furnace slag	-
Oil shale	-
Trass	-

*BPG: Fuels from production-specific industrial wastes
*SBS: Substitute fuels from municipal wastes

Table A2: **Average values and ranges of trace element concentrations of the input materials, intermediate and final products compiled from miscellaneous sources. Selection of investigated input materials according to the input materials cited by the VDZ [VDZ, 2001].**

Data in ppm		As	Be	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Se	Sn	Te	Tl	V	Zn
Limestone	Min	0.1	0.01	0.02	0.1	0.5	5	0.005	250	1.4	0.27	0.2	0.4	0.9		0.05	5	0.1
	Max	15	12	2	7	184	57	0.1	3300	131	151	27	30	24		3	80	229
	AV	**3**	**0.3**	**0.2**	**3**	**14**	**11**	**0.04**	**500**	**18**	**18**	**1**	**0.6**	**4**	**0.7**	**0.3**	**26**	**30**
Marl	Min	0.2		0.02		1.2	4.9	0.005		1.5	0.3					0.05		22
	Max	12	1	0.5	28	71	35	0.1	3300	57	57	27		24		0.68	49	79
	AV	**6**	**0.5**	**0.3**	**5**	**28**	**12**	**0.03**	**360**	**16**	**12**	**4**	**1**	**3**	**1**	**0.6**	**20**	**48**
Clay	Min	2	1	0.01	6	15	10	0.01		7	1	0.5		1.6		0.1	30	2
	Max	100	7	1	25	260	285	0.5	2500	236	219	13	2.5	30		1.6	300	304
	AV	**14**	**3**	**0.2**	**20**	**85**	**43**	**0.2**	**600**	**63**	**25**	**2**	**0.5**	**5**	**0.5**	**0.5**	**130**	**78**
Sand	Min	0.4	0.6	0.01	0.3	1	1.2	0.01	46	1	0.7	0.3		1.8		0.05	2	4.2
	Max	42	1.5	1	37	220	85	1	2040	73	70	12		40		1	240	112
	AV	**11**	**1.0**	**0.2**	**11**	**19**	**10**	**0.02**	**194**	**13**	**10**	**7**	**1**	**3**	**0.5**	**0.2**	**50**	**25**
Materials from iron and steel works[1]	Min	2	0.8	0.02	10	8	20	0.04	71	5	4	1	0.7	6	2	0.07	10	24
	Max	1200	2.0	17900	450	200000	12600	10	46479	80000	570000	37	600	800	13	400	3000	350000
	AV	151	2.8	109	191	3284	1872	2	7488	830	4698	24	127	278	9	3	442	21641
	xMin	**74**	**1.9**	**29**	**149**	**600**	**1076**	**0.4**	**4605**	**254**	**481**	**10**	**15**	**81**	**2**	**0.4**	**229**	**2262**
Iron ore	Min	2	0.8	0.02	109	8			900	5	4					0.1	10	24
	Max	1200	2	15	183	1400		1	1200	815	8700			500	13	400	690	9400
	AV	**37**	**1**	**6**	**144**	**495**	**1520**	**0.5**	**1090**	**331**	**350**	**26**	**8**	**25**	**10**	**2**	**256**	**3288**
Ashes from burning processes[2]	Min	0.5	0.2	0.11	2.3	36	4.4	0.003	60	6.8	4.7		1	8.9	0.1	0.5	1	5
	Max	42	3.6	2.3	15	450	110	1.4	285	240	200	2.5	10	15	10	2.6	64	470
	AV	**6.6**	**1.3**	**0.6**	**5.5**	**190**	**32**	**0.3**	**110**	**23**	**25**	**2**	**1**	**12**	**1**	**0.7**	**2.3**	**94**
Foundry sand	Min	0.5		0.05		1	5	0.03		1	1					0.1		3
	Max	10	3	2	150	650	200	4.4		300	200	1	1	50		4.4	200	553
	AV	**3**	**2**	**0.3**	**90**	**290**	**28**	**0.3**		**92**	**62**	**0.8**	**0.8**	**40**		**0.5**	**150**	**75**
Hard coal	Min	1	0	0.01	0.5	1	0.30	0.01	5	1	5	0.05	0	1.3	0.2	0.1	10	4.5
	Max	200	8	10	43	260	60	3	356	110	270	5	6	7.8	5.0	5	250	405
	AV	**9**	**1.4**	**1.0**	**9**	**14**	**18**	**0.3**	**58**	**23**	**27**	**1**	**2**	**4**	**2**	**1**	**39**	**63**
Brown coal	Min	0.1	0.04	0.06	0.5	0.9	0.4	0.01	50	0.6	0.7	0.04	0.4	0.5	0.1	0.05	0.1	1
	Max	12	0.6	2.4	4.2	20	15	0.7	160	29	34	2.5	25	15	10	0.4	84	70
	AV	**0.8**	**0.2**	**0.2**	**1**	**3.6**	**1.8**	**0.2**	**77**	**3**	**3**	**0.8**	**2.6**	**4**	**3**	**0.1**	**10**	**10**
Oil coke	Min	0.2	0.02	0.04		0.9		0.01		24	1					0.04	45	16
	Max	0.8	0.03	4		104		0.09		355	102					3.1	1435	220
	AV	**0.5**	**0.03**	**1**	**2.5**	**4.3**	**2.4**	**0.05**		**263**	**13**	**0.6**		**0.3**		**0.5**	**758**	**16**
Used tyres	Min	0.1	0.02	0.1	5	5	10	0.1	6	17	3	1		4		0.2	1	14
	Max	20	0.5	20	207	640	300	1	890	380	760	410		20		50	60	20500
	AV	**1.6**	**0.3**	**7**	**30**	**137**	**68**	**0.4**	**189**	**90**	**125**	**136**	**4**	**15**		**10**	**19**	**6100**
Waste oil	Min	0.01		0.2	0.2	1	5	0.01	5	1	2		1	5	1	0.02	0.9	1
	Max	100		15	15	290	640	2	29	150	5000	2	5	8	5	5	39	4800
	AV	**2.4**	**0.6**	**0.8**	**1**	**12**	**51**	**0.3**	**15**	**20**	**151**	**1**	**3**	**6**	**3**	**0.5**	**2**	**700**
Scrap wood	Min	0.5		0.05		0.2	0.9	0.01		0.5	0.1		2	2.2		0.5		1.4
	Max	22	2	24	15	192	160	1	200	264	1776	10	20	50		2	5	3143
	AV	**3.4**	**0.5**	**1.2**	**10**	**27**	**24**	**0.2**	**150**	**13**	**222**	**8**	**5**	**6**		**0.8**	**3**	**440**
Fractions from municipal, commercial and industrial waste	Min	0.05	0.2	0.5	0.5	1	8.1	0	8.4	2.5	5		5	5	1	0.05	0.5	19
	Max	11	3.3	11	13	293	655	1.4	524	281	325	2020	33	116	33	0.4	35	1280
	AV	**3**	**0.9**	**2.5**	**4**	**51**	**138**	**0.3**	**109**	**25**	**74**	**25**	**8**	**20**	**7**	**0.1**	**7**	**331**
Meat and bone meal	AV	**0.5**	**0.1**	**0.4**	**2**	**6**	**26**	**0.2**		**3**	**3**					**0.5**		**140**
Gypsum/ Anhydrite[3]	Min	0.2	0.02	0.03	0.02	1	0.3	0.00625		0.3	0.2	0.1	0.6			0.1	1	1
	Max	3.5	0.9	2.3	3.9	27.3	12.8	1.3		14.5	20.5	5	17			1.0	27.8	59
	AV	**1.5**	**0.2**	**0.15**	**1**	**8.8**	**7**	**0.1**		**5.5**	**7**	**1**	**0.8**			**0.3**	**13.5**	**19**
Blast-furnace slag	Min			0.01	2	1	2	0.01	1000	1	1					0.2		1
	Max	1		1	8	75	10	1	8000	10	21		2			1	50	280
	AV	**0.8**		**0.7**	**4**	**25**	**5.2**	**0.6**	**3500**	**5**	**6**	**2**	**1.5**	**5**		**0.7**	**30**	**38**
Oil shale	Min	3		0.05		20	26	0.05			10					0.1		85
	Max	37		3		117	95	0.3			50					7		270
	AV	**10**		**1.5**		**60**	**60**	**0.2**			**38**					**2**		**190**
Coal fly ash	Min	5	5	0.2	11.7	29	41.6	0.04	71	26	7	1	0.7	6		0.2	122	51
	Max	321	40	34	101	330	652	2.4	1180	600	800	37	35	64		29	940	1200
	AV	**79**	**15**	**2.6**	**74**	**172**	**247**	**0.3**	**484**	**196**	**257**	**14**	**8**	**10**	**1.6**	**4**	**345**	**504**

Min = Minimum value; Max = Maximum value; AV = Average value

Continuation: Average values and ranges of trace element concentrations of the input materials, intermediate and final products compiled from miscellaneous sources. Selection of investigated input materials according to the input materials cited by the VDZ [VDZ, 2001].

		As	Be	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Se	Sn	Te	Tl	V	Zn
Raw meal	Min	1.6	0.1	0.03	3	23	5	0.008	50	12	1.7	0.1	0.7	2	0.1	0.1	6	10
	Max	28	2.5	1.1	14	59	19	1	500	38	98	2.3	30	10	10	12	120	108
	AV	**9**	**1**	**0.3**	**7**	**30**	**14**	**0.06**	**236**	**20**	**14**	**0.7**	**1.3**	**3**	**1**	**0.5**	**37**	**34**
Clinker	Min	2	0.2	0.01	6	10	5	0,001	218	10	1	0,1	0.2	1	0.2	0.01	10	29
	Max	87	2	4	48	422	136	1.2	526	397	105	17	20	36	1	10	136	600
	AV	**9**	**1.4**	**1**	**13**	**66**	**38**	**0.1**	**400**	**38**	**24**	**5**	**4**	**13**	**0.6**	**0.5**	**57**	**113**
Portland cement	Min	2	0.2	0.03	3	25	14	0.02	107	14	5	0.5		1		0.02	15	21
	Max	117	1.6	6	21	712	98	0.5	3901	97	254	18		14		4.1	144	679
	AV	**8**	**1**	**0.6**	**11**	**68**	**38**	**0.3**	**606**	**45**	**27**	**5**		**3**		**0.6**	**74**	**164**
Blastfurnace cement	Min	0.8		0.1	0.2	19	5			4	1						62	5
	Max	15		1	18	246	160			53	136						444	245
	AV	**6**	**3**	**0.5**	**6**	**50**	**13**	**0.1**		**17**	**13**	**5**				**0.5**	**113**	**122**

[1]: Materials from iron and steel works are compiled of pyrite cinder, contaminated ore, iron oxide / fly ash mixtures, dusts from steel works and mill scale. Since data on trace element concentrations of contaminated ore no were not available, trace element concentrations of iron ore were used for calculations instead. For the item „iron oxide / fly ash mixtures“ trace element concentrations of coal fly ash were used instead. For the compilation of trace element concentrations of the total item „materials from iron and steel works“ the amounts of each individual item were considered. However, rather than using average values for performing the material flow calculations, average minimum values derived from the literature data were used. Furthermore, for the calculation of these average minimum values, highly loaded dusts, ores, fly ashes etc. were not taken into consideration, since it may be assumed that these materials are not used as input materials for the production of cement.

[2]: Since ashes from burning processes are not further specified, it was assumed that the composition of these ashes will resemble the one of bottom ashes from brown coal. Therefore, trace element concentrations from brown coal bottom ashes were applied for the item “ashes from burning processes”.

[3]: Since in the literature data on trace element concentrations of “gypsum” in general are seldom specified in gypsum or anhydrite, trace element concentrations of gypsum and anhydrite could not be distinguished. Therefore, it was assumed that both items contain the same trace element concentrations and they were compiled to one item. Trace element concentrations of FGD-gypsum are available. For calculations concerning the top-down and bottom-up approach a new item “gypsum” was compiled consisting of 75 % gypsum / anhydrite and 25 % FGD-gypsum regarding its trace element concentration.

Table A3: Amounts of input materials used for clinker production and cement grinding in Germany in the year 1999. In accordance to the „Umweltdaten“ of the VDZ [VDZ, 2001].

	Input material	Input for clinker production [t/a]	Input for cement grinding [t/a]	Total input [t/a]
Primary raw materials*	**Limestone**	35,695,913	904,087	36,600,000
	Marl	10,000,000		10,000,000
	Clay incl. Bentonite/Caolinite	1,985,000		1,985,000
	Sand	1,240,000		1,240,000
Secondary raw materials**	**Materials from iron and steel works**	170,000		170,000
	Iron ore	117,000		117,000
	Ashes from burning processes	240,000		240,000
	Coal fly ash	212,039	87,961	300,000
	Foundry sand	140,000		140,000
Primary fuels ***	**Hard coal**	980,000		980,000
	Brown coal	2,140,000		2,140,000
	Oil coke	312,903		312,903
Secondary fuels ***	**Used tyres**	236,000		236,000
	Waste oil	181,000		181,000
	Scrap wood	77,000		77,000
	Fraction from commercial, municipal and industrial waste	290,000		290,000
Interground additives ****	**Gypsum/Anhydrite**		1,305,000	1,305,000
	FGD Gypsum		420,000	420,000
	Blast-furnace slag		4,900,000	4,900,000
	Oil shale	96,275	259,725	356,000
	Trass	2335	94,665	97,000

Continuation of Table A3: Remarks concerning the differences between the amounts of input materials listed above and the amounts listed in the „Umweltdaten 2001“ by the VDZ [VDZ, 2001]:

* Primary raw materials: a total sum of 46,600 t/a is cited by the VDZ for limestone / marl / chalk without differentiation. For distinction between the individual raw materials it was assumed that chalk is applied in a few plants only and therefore negligible. The ratio limestone to marl was estimated to be 3.6 to 1.

On the other hand the VDZ distinguishes between clay and bentonite / caolinite. In this study, these two items were aggregated to one general item "clay".

** Secondary raw materials: materials from iron and steel works are compiled as follows: pyrites cinder 47,000 t/a; contaminated ore 30,000 t/a; iron oxide / fly ash mixtures 10,000 t/a; dusts from steel works 38,000 t/a; mill scale 38,000 t/a; 7,000 t/a others.

Since ashes from burning processes were not further specified, it was assumed that the composition of these ashes will resemble the one of bottom ashes from brown coal. Therefore, trace element concentrations from brown coal bottom ashes were applied for the item "ashes from burning processes".

Another item from the category "secondary raw materials" cited by the VDZ, the "paper residues" with an annual amount of 172,000 t was excluded from the calculations due to lack of data on trace element concentrations.

*** Regular fuels and secondary fuels: the fuels were converted from MJ/a to t/a according to their calorific value.

**** Interground additives: the VDZ differentiates between gypsum, anhydrite and FGD-gypsum. Since in the literature data on trace element concentrations of "gypsum" are seldom specified in gypsum or anhydrite, trace element concentrations of gypsum and anhydrite could not be distinguished. Therefore, it was assumed that both items contain the same trace element concentrations and they were compiled to one item.

While performing the compilation of the different cement types according to the production statistics (VDZ) and the cement standard (DIN EN 197-1), excessive amounts of coal fly ash, trass and oil shale occurred which are not used as interground additives and were therefore attributed to the clinker production.

Table A4: **Production statistics for Germany in 1999. Data derived from "Umweltdaten der deutschen Zementindustrie" [VDZ, 2001] and from "Zahlen und Daten 1998/1999" [BDZ, 1999].**

Clinker production	27739000	t/a
Cement production	36200000	t/a
Domestic sales	33776000	t/a

Type of cement	Group	Unit	Domestic sales	**Cement production**	Share of total production
Portland cement	CEM I	t/a	22131000	**23719274**	65.5%
Slag cement	CEM II	t/a	4417000	**4733995**	13.1%
Pozzolanic cement		t/a	143000	**153263**	0.4%
Shale cement		t/a	412000	**441568**	1.2%
Limestone cement		t/a	1852000	**1984912**	5.5%
Blastfurnace cement	CEM III	t/a	4651000	**4984788**	13.8%
Others		t/a	170000	**182200**	0.5%
Total		t/a	33776000	**36200000**	100%

Table A5: **Contribution of individual classes of input materials (in %) to the total trace element concentration of Portland cement and „mixed cement".**

Portland cement

	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sb	Sn	Tl	V	Zn
Primary raw materials	78	48	65	71	52	94	76	70	62	78	68	74	38
Primary fuels	4	8	4	2	2	1	9	3	2	5	4	15	3
Secondary fuels	1	12	5	4	6	0.4	3	8	28	5	19	0	37
Secondary raw materials	14	29	24	21	37	4	11	16	6	11	5	9	20
Interground additives	3	3	2	2	3	0.1	1	3	2	0.2	4	2	2

"Mixed cement"

	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sb	Sn	Tl	V	Zn
Primary raw materials	75	41	60	64	50	54	73	66	58	70	59	67	36
Primary fuels	4	8	4	2	2	1	8	3	2	5	3	14	2
Secondary fuels	1	10	5	3	6	0	3	8	26	4	16	0	35
Secondary raw materials	13	24	22	19	35	3	11	15	5	10	5	8	19
Interground additives	7	17	9	12	7	42	5	8	9	11	17	11	8

Table A6: **Bottom-up approach: average values and ranges of trace element concentrations in Portland cement and blastfurnace cement and contributions of individual input paths to these total concentrations. Application of the bottom-up scenarios A, B and C.**

Portland cement

		Arsenic			Cadmium			Cobalt			Chromium		
Scenario		**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**
Raw meal		**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Fuel		**brown coal**	**brown coal**	**hard coal**	**brown coal**	**brown coal**	**fuel-mix 3**	**brown coal**	**brown coal**	**fuel-mix 2**	**brown coal**	**brown coal**	**fuel-mix 3**
Concentration in Portland cement (ppm)	Concentration range	4-13	5-14	8-18	0.2-0.6	0.2-0.7	0.7-1.4	5-14	7-16	10-19	30-57	37-64	47-73
	Average value	8	9	12	0.4	0.5	1.0	9	11	15	43	50	60
Share as input pathway (%)	Prim. RM	94	86	76	81	63	36	95	74	70	96	80	71
	Prim. Fuel	3	3	9	15	11	6	3	2	6	2	2	1
	Sec. Fuel	0	0	0	0	0	30	0	0	6	0	0	10
	Sec. RM	0	8	8	0	23	28	0	22	17	0	16	15
	IA	3	3	7	4	3	1	2	2	1	2	2	1

		Copper			Manganese			Nickel			Lead		
Scenario		**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**
Raw meal		**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Fuel		**brown coal**	**brown coal**	**fuel-mix 3**	**hard coal**	**hard coal**	**fuel-mix 3**	**brown coal**	**brown coal**	**fuel-mix 1**	**brown coal**	**brown coal**	**fuel-mix 4**
Concentration in Portland cement (ppm)	Concentration range	16-41	33-72	46-80	342-1344	350-1341	388-1357	28-54	32-59	41-68	17-48	22-53	36-72
	Average value	27	51	62	779	784	817	41	46	54	30	36	52
Share as input pathway (%)	Prim. RM	95	51	50	99	96	91	97	85	79	94	78	67
	Prim. Fuel	2	1	2	1	1	1	2	2	11	3	2	3
	Sec. Fuel	0	0	13	0	0	2	0	0	0	0	0	15
	Sec. RM	0	47	34	0	3	7	0	12	9	0	17	14
	IA	4	2	1	0	0	0	2	2	1	3	3	2

		Antimony			Tin			Vanadium			Zinc		
Scenario		**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**
Raw meal		**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Fuel		**fuel-mix 1**	**fuel-mix 1**	**fuel-mix 3**	**hard coal**	**hard coal**	**fuel-mix 3**	**brown coal**	**brown coal**	**fuel-mix 1**	**brown coal**	**brown coal**	**fuel-mix 3**
Concentration in Portland cement (ppm)	Concentration range	0.7-3.5	1.1-3.9	3.6-12.5	3.3-11.3	3.5-11.3	5.1-13.1	50-95	52-96	70-119	32-100	64-178	177-471
	Average value	2.0	2.4	7.3	6.7	7.0	8.7	73	75	95	63	115	297
Share as input pathway (%)	Prim. RM	85	70	33	91	85	69	95	89	78	92	51	26
	Prim. Fuel	9	7	1	9	8	3	3	3	16	4	2	1
	Sec. Fuel	0	0	60	0	0	17	0	0	0	0	0	56
	Sec. RM	0	19	5	0	7	11	0	6	4	0	44	17
	IA	6	4	1	0	0	0	2	2	1	4	2	1

Blastfurnace cement

		Arsenic		Cadmium		Cobalt		Chromium		Copper		Manganese	
Scenario		**A**	**C**	**A**	**C**	**A**	**C**	**A**	**C**	**A**	**C**	**A**	**C**
Raw meal		**1**	**3**	**1**	**3**	**1**	**3**	**1**	**3**	**1**	**3**	**1**	**3**
Fuel		**brown coal**	**hard coal**	**brown coal**	**fuel-mix 3**	**brown coal**	**fuel-mix 2**	**brown coal**	**fuel-mix 3**	**brown coal**	**fuel-mix 3**	**hard coal**	**fuel-mix 3**
Concentration in cement	Concentration	1-3	2-4	0.2-1.1	0.3-1.2	3-7	4-8	18-37	20-40	6-12	11-18	952-5475	956-5479
	Average value	2	3	0.6	0.7	5	6	27	30	9	14	2923	2929
Share as input pathway (%)	Prim. RM	62	59	11	10	33	31	26	24	48	35	7	7
	Prim. Fuel	2	7	2	2	1	3	1	0	1	1	0	0
	Sec. Fuel	0	6	0	8	0	8	0	5	0	24	0	0
	Sec. RM	0	0	0	8	0	2	0	3	0	9	0	0
	IA	36	28	87	72	66	56	74	67	51	31	93	93

		Nickel		Lead		Antimony		Tin		Vanadium		Zinc	
Scenario		**A**	**C**	**A**	**C**	**A**	**C**	**A**	**C**	**A**	**C**	**A**	**C**
Raw meal		**1**	**3**	**1**	**3**	**1**	**3**	**1**	**3**	**1**	**3**	**1**	**3**
Fuel		**brown coal**	**fuel-mix 1**	**brown coal**	**fuel-mix 4**	**fuel-mix 1**	**fuel-mix 3**	**hard coal**	**fuel-mix 3**	**brown coal**	**fuel-mix 1**	**brown coal**	**fuel-mix 3**
Concentration in cement	Concentration	8-14	10-16	6-14	9-18	0.6-3.9	1.2-4.7	2.1-8.9	2.4-9.1	25-48	28-52	19-70	46-121
	Average value	11	13	10	13	2	2.8	5.1	5.4	36	39	41	78
Share as input pathway (%)	Prim. RM	59	53	47	42	21	15	25	23	32	31	28	16
	Prim. Fuel	1	7	1	2	2	0	2	1	1	6	1	1
	Sec. Fuel	0	6	0	9	0	2	0	3	0	2	0	10
	Sec. RM	0	0	0	9	0	30	0	5	0	0	0	35
	IA	40	33	52	38	77	52	73	68	67	61	71	38

Prim. RM = primary raw materials; Prim. fuel = primary fuel; Sec. RM = secondary raw materials; Sec. fuel = secondary fuel

For description of raw meal and fuel composition see Table 9

Table A7: **Bottom-up approach: average values and ranges of trace element concentrations in Portland cement and contributions of individual input paths to these total concentrations. Application of the bottom-up scenarios C and D.**

Portland cement

		Cadmium		Cobalt		Chromium	
Scenario		D	C	D	C	D	C
Raw meal		**2**	**3**	**2**	**3**	**2**	**3**
Fuel		**Fuel-mix3**	**Fuel-mix3**	**Fuel-mix2**	**Fuel-mix2**	**Fuel-mix3**	**Fuel-mix3**
Concentration in Portland cement (ppm)	Concentration range	0.5-1.1	0.7-1.4	9-18	10-19	42-70	47-73
	Average value	0.8	1.0	13	15	56.0	59.5

		Copper		Manganese		Lead	
Szenario		D	C	D	C	D	C
Rohmehl		**2**	**3**	**2**	**3**	**2**	**3**
Fuel		**Fuel-mix3**	**Fuel-mix3**	**Fuel-mix3**	**Fuel-mix3**	**Fuel-mix4**	**Fuel-mix4**
Concentration in Portland cement (ppm)	Concentration range	41-81	46-80	358-1352	388-1357	28-60	36-72
	Average value	59	62	791	817	43	52

		Antimony		Tin		Zinc	
Szenario		D	C	D	C	D	C
Rohmehl		**2**	**3**	**2**	**3**	**2**	**3**
Fuel		**Fuel-mix3**	**Fuel-mix3**	**Fuel-mix3**	**Fuel-mix3**	**Fuel-mix3**	**Fuel-mix3**
Concentration in Portland cement (ppm)	Concentration range	3.4-12.5	3.6-12.5	4.5-12.9	5.1-13.1	162-466	177-471
	Average value	7	7	8	9	292	297

Prim. RM = primary raw materials; Prim. fuel = primary fuel; Sec. RM = secondary raw materials; Sec. fuel = secondary fuel

For description of raw meal and fuel composition see Table 9

Table A8: **Trace element concentrations (in ppm) of various input materials used for the calculation of trace element concentrations in concrete.**

	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sn	Tl	V	Zn
Coal fly ash	79	2.6	74	172	247	484	196	257	10	4	345	504
Sand/Gravel	5	0.2	7	26	10	77	7	10	3	0.2	18	11
Basalt	5	1	35	215	44	1402	97	10	3		200	102
Slag	5	1	7	300	150	30000	30	20	17	1.5	600	250
Water*	0,01	0.005		0,05	2		0.02	0.01				

* according to the German Drinking Water Regulation

Table A9: **Trace element concentrations of cement filter dusts compiled from miscellaneous sources.**

Data in ppm		As	Be	Cd	Co	Cr	Cu	Hg	Mn
Filter dust cement	Minimum value	0.03	0.1	0.003	2.7	0.03	0.08	0.002	107
	Maximum value	90	1.7	18	7.9	81	194	0.7	312
	Average value	**25**	**1.1**	**7**	**11**	**51**	**15**	**0.4**	**273**

		Ni	Pb	Sb	Se	Sn	Te	Tl	V	Zn
Filter dust cement	Minimum value	0.01	0.4	1	1	1	1	5	22	0.6
	Maximum value	340	445	6	8	35	1.8	75	3584	362
	Average value	**21**	**137**	**3**	**4**	**10**	**1.4**	**46**	**67**	**91**

Table A10: Average trace element concentration and concentration ranges of four concrete variants and shares of individual input materials in the total content. Variants 1 and 2 with Portland cement and blastfurnace cement and sand / gravel aggregates.

		Concrete from blastfurnace cement and gravel/sand aggregates						Concrete from Portland cement and gravel/sand aggregates					
		%*	%*	%*	%*	%*	ppm	%*	%*	%*	%*	%*	ppm
		Blast-furnace cement	Water	Coal fly ash	Gravel	Sand	Concrete	Portland cement	Water	Coal fly ash	Gravel	Sand	Concrete
Arsenic	10Perc	5	0	10	12	10	3.5	12	0	9	11	9	4.2
	90Perc	15	0	48	55	50	8.9	31	0	41	48	44	9.8
	AV	9	0	28	34	30	6.0	21	0	24	29	26	6.8
Cadmium	10Perc	17	0	6	9	8	0.2	23	0	6	9	7	0.2
	90Perc	53	0	33	45	41	0.4	50	0	31	42	38	0.4
	AV	33	0	18	26	23	0.3	36	0	17	25	22	0.3
Cobalt	10Perc	6	0	7	15	13	5	11	0	6	14	11	5
	90Perc	20	0	37	57	52	11	30	0	35	53	48	12
	AV	12	0	21	35	32	8	19	0	19	33	29	8
Chromium	10Perc	11	0	7	25	20	22	17	0	7	23	19	24
	90Perc	22	0	20	50	46	35	29	0	18	47	43	38
	AV	16	0	13	37	33	28	23	0	12	34	31	30
Copper	10Perc	9	0	13	10	8	10	21	0	10	8	7	13
	90Perc	23	2	55	45	41	21	45	2	45	37	34	25
	AV	16	1	33	27	24	15	32	1	27	21	19	19
Manganese	10Perc	62	0	1	2	2	194	41	0	2	5	4	115
	90Perc	94	0	6	18	16	845	79	0	11	32	28	281
	AV	81	0	3	9	8	473	61	0	6	18	15	189
Nickel	10Perc	14	0	23	15	13	9	32	0	16	11	9	12
	90Perc	24	0	47	34	32	14	48	0	35	26	24	19
	AV	18	0	35	25	22	12	39	0	26	18	16	16
Lead	10Perc	9	0	14	10	8	10	20	0	11	8	7	13
	90Perc	25	0	55	45	41	21	47	0	46	37	35	25
	AV	16	0	34	26	24	15	32	0	27	21	19	19
Tin	10Perc	11	0	2	15	12	2	18	0	2	13	10	2
	90Perc	43	0	13	58	54	5	50	0	12	52	48	5
	AV	25	0	7	36	32	3	33	0	6	32	28	4
Vanadium	10Perc	15	0	17	17	14	21	25	0	15	15	12	24
	90Perc	29	0	37	38	35	33	39	0	33	33	31	38
	AV	22	0	27	27	24	27	32	0	23	24	21	31
Zinc	10Perc	20	0	15	5	5	18	40	0	10	3	3	29
	90Perc	51	0	56	28	27	40	70	0	41	20	19	55
	AV	35	0	35	16	14	28	55	0	24	11	10	41
		*Share of total content						*Share of total content					

Continuation Table A10: **Average trace element concentration and concentration ranges of four concrete variants and shares of individual input materials in the total content.** Variants 3 and 4 with Portland cement and blastfurnace cement and basalt / slag aggregates.

		Concrete from blastfurnace cement and basalt/slag aggregates						Concrete from Portland cement and basalt/slag aggregates					
		%*	%*	%*	%*	%*	ppm	%*	%*	%*	%*	%*	ppm
		Blast-furnace cement	Water	Coal fly ash	Basalt	Slag	Concrete	Portland cement	Water	Coal fly ash	Basalt	Slag	Concrete
Arsenic	10Perc	4	0	10	12	11	3.5	11	0	9	11	10	4.3
	90Perc	14	0	47	55	53	9.1	30	0	40	48	47	9.9
	AV	9	0	26	34	32	6.1	20	0	23	29	28	6.8
Cadmium	10Perc	4	0	2	18	14	0.5	6	0	2	19	15	0.5
	90Perc	22	0	13	66	63	1.4	21	0	13	67	63	1.5
	AV	12	0	6	43	39	0.9	13	0	6	43	38	0.9
Cobalt	10Perc	2	0	2	48	4	9	4	0	2	45	4	9
	90Perc	10	0	19	87	29	31	16	0	18	86	28	32
	AV	5	0	9	69	16	19	9	0	9	67	15	20
Chromium	10Perc	1	0	1	28	36	144	2	0	1	27	36	147
	90Perc	3	0	3	60	69	278	5	0	3	59	68	281
	AV	2	0	2	43	53	207	3	0	2	42	53	209
Copper	10Perc	1	0	2	8	39	41	4	0	2	8	37	44
	90Perc	5	0	15	48	84	131	13	0	14	44	82	135
	AV	3	0	7	25	65	81	8	0	7	23	62	84
Manganese	10Perc	1	0	0	1	76	4161	0	0	0	1	81	3948
	90Perc	9	0	0	15	97	22123	3	0	0	16	98	22093
	AV	5	0	0	7	88	12063	1	0	0	7	91	11797
Nickel	10Perc	2	0	4	56	11	38	7	0	4	51	10	42
	90Perc	5	0	12	80	31	75	14	0	11	76	29	79
	AV	4	0	7	69	20	57	10	0	7	64	19	61
Lead	10Perc	7	0	10	8	16	11	15	0	8	7	13	15
	90Perc	20	0	48	39	60	28	40	0	41	33	53	31
	AV	13	0	27	22	38	19	26	0	23	19	32	22
Tin	10Perc	4	0	1	5	44	4	6	0	1	5	39	4
	90Perc	20	0	6	32	88	14	27	0	6	32	85	15
	AV	11	0	3	17	69	8	15	0	3	16	66	9
Vanadium	10Perc	1	0	1	15	53	211	2	0	1	15	53	215
	90Perc	3	0	4	41	82	438	4	0	4	40	81	443
	AV	2	0	2	27	69	316	3	0	2	27	68	320
Zinc	10Perc	3	0	2	10	28	77	7	0	2	9	25	88
	90Perc	12	0	15	51	79	248	25	0	14	47	75	257
	AV	7	0	8	29	56	153	15	0	7	27	52	165
		*Share of total content						*Share of total content					

Trace element contents of Portland cement, Portland cement clinker, clinker minerals and dust

In the following table A11 trace element contents of individual materials stemming from the cement burning process are set up from literature. Additionally trace element contents of the final product Portland cement are given (complemented by own analyses, see section 2.5). As far as a batch-wise discharge of an element with technical clinker is observed which indicates the formation of trace element rich accretions in the rotary kiln, this is recorded.

Further, the trace element content of individual clinker phases is important. Since the particular trace element contents in technical clinkers are too low for a direct analytical proof, only data on maximum solubilities of some trace elements in the main clinker phases are available from laboratory experiments.

Analyses from different sources indicated in table A11 (in particular single analyses) are not directly comparable among one another since they depend strongly on the operating parameters in different part of the cement plant (temperature, input of raw material and/or fuel, redox conditions) and from the compositions of the raw materials, which vary strongly. For this reason, in addition mean trace element contents specified for Portland cement, cement clinkers and filter dusts in the material flow analytical part of this work are given (see also table A2 and table A9 in the appendix). In particular for the calculation of mean contents of filter dusts, confidential data sources were also used.

Table A11: **Trace element contents (ppm) of ordinary Portland cement (OPC), Portland cement clinker (clinker), electrostatic precipitator ash (EPA) and CKD (USA). Additionally maximum trace element solubilities of important clinker minerals are given (in Weight% of element). + : crystal chemical incorporation proofed; --: no crystal chemical incorporation. ∅: mean content. Numbers in italics: US-American sources. Underlined: single analysis, secondary fuel used. Bold: Mean contents used for calculations (Source: Table A2, Table A9).**

[1] VDZ (2001); [2] Bhatty (1995); [3] Scur (2002); [4] Germaneau et al. (1993); [5] Moir and Glasser (1992); [6] Schreiber and Smeenk (1998); [7] Krcmar (1991); [8] Mallonn et al. (1988); [9] Cohen (1995); [11] Gierzatowicz (2000); [12] Gossmann et al. (1990); [13] Locher (2000); [14] Hohberg and Schießl (1995); [15] Karstensen (1994); [16] Murat and Sorrentino (1996a); [17] Murat and Sorrentino (1996b); [18] Kirchner (1985); [19] Weisweiler et al. (1987); [20] Hornain (1971); [21] van der Sloot (2001); [22] Sprung (1982); [23] own analysis.

	OPC (ppm)	Clinker (ppm)	CKD (ppm)	EPA (ppm)	C_3S (wt.%)	C_2S (wt.%)	C_3A (wt.%)	C_4AF (wt.%)
As	<1-50[1] ∅6.8[1] *∅19*[2] 6[3] <14-110[23] ∅34[23] **∅8**	13-117[4] ∅42.4[5] **∅9**	*∅18*[2] *∅6.9*[6] *∅34.3*[6] *∅20.4*[6] *∅13*[6] *∅23.8*[6]	∅28.5[7] ∅12.0[8] ∅16[9] ∅0.2-0.5[22] **∅25**	0.45[11]			
	Possibly as $Ca_3(AsO_4)_2$. *Batch-wise discharge*[12].							
Ba	*∅280*[2] 185-390[14]		*∅172*[2]	70[15]	2[11]	0.27[11]		
Be	<0.2-2.5[1] ∅0.7[1] 0.3-2[23] ∅1[23] **∅1**	**∅1.4**	*∅0.71*[6] *∅0.517*[6] *∅3.9*[6] ∅*0.645* [6]	∅<1[9] **∅1.1**				
Bi	1-5[14]							
Cd	<0.1-8[1] ∅0.4[1] *∅0.34*[2] 0.5[3] **∅0.6**	0.1-1.7[4] ∅0.44[5] laboratory: 1.7%[16],[17] **∅1**	*5-10*[12] *∅13.2*[6] *∅8.05*[6] *∅18.6*[6] *∅8.83*[6] *∅20.0*[6]	∅18.4[7] ∅21[8] ∅14[9] **∅7**	+[18] +[19] 0.6[16]	+[18] +[19] 0.26[16]	$C_{12}A_7$: 3.3[16]	0.14[16]
	In laboratory clinker as (Ca,Cd)O[16].							
Co	1-28[1] ∅10[1] *<130*[2] 2-11[23] ∅7[23] **∅11**	10-14[15] **∅13**		∅7.9[7] 12[15] **∅11**	0.4[20]	0.25[20]	0.5[20]	4[20]
Cr	20-100[1] ∅40[1] *20-450*[2] 45[3] 10-60[23] ∅31[23] **∅68**	60-155[4] ∅70.5[5] laboratory: 2.6%[16],[17] **∅66**	*0.01-299*[2] *∅26.6*[6] *∅39*[6] *∅35.9*[6] *∅40.8*[6] *∅41.6*[6]	∅71.5[7] ∅79.82[8] ∅81[9] **∅51**	1.2[16] 0.57[20] 0.73[11]	3.25[16] 1.11[20] 0.42[11]	0.1[20]	0.5[20]

	OPC (ppm)	Clinker (ppm)	CKD (ppm)	EPA (ppm)	C_3S (wt.%)	C_2S (wt.%)	C_3A (wt.%)	C_4AF (wt.%)
Cu	0-300[1] ∅25[1] 100[3] 9-41[23] ∅21[23] **∅38**	∅43.9[5] *∅90*[2] **∅38**	*-500*[2] *∅28.4[6]* *∅30.1[6]*	∅32.3[7] **∅15**	0.7[20]	0.2[20]	0.4[20]	1.1[20]
Hg	<0.02-0.35[1] ∅0.07[1] 0.1[3] **∅0.3**	0.03-0.1[4] **∅0.12**	*∅1[6]* *∅0.104[6]* *∅0.1[6]* *∅17.3[6]*	0.19[15]. ∅0.7[9] **∅0.4**				
Mo	1-8[21]<1-5[23] ∅ 2[23]			<4[15]				
Ni	20-80[1] ∅24[1] *∅31*[2] 9-41[23] ∅20[23] **∅45**	18-49[4] **∅38**	*-60*[2]*∅19[6]* *∅18.3[6]* *∅0.49[6]* *∅19.3[6]*	∅339.8[7] ∅3[9] **∅21**	0.5[20]	0.25[20]	0.3[20]	3[20]
Pb	0-200[1] ∅27[1] 35[3] 12-106[23] ∅41[23] **∅27**	8.7-171[4] ∅14.9[5] *12*[2] laboratory: 0%[16],[17] **∅24**	*434*[2] *70-445[12]* *∅388.4[6]* *∅210.3[6]* *∅283.7[6]* *∅434.5[6]* *∅252.9[6]*	∅2376.1[7] ∅1151.3[8] ∅842[9] ∅1.7-11[22] **∅137**	--[16]	--[16]		
	Batch-wise discharge [12].							
Sb	<1-35[1] ∅6.0[1] - *4*[2] **∅5**	**∅5**	*-3.4*[2] *∅7.7[6]* *∅0.53[6]* *∅112.8[6]* *∅0.395[6]* *∅3.3[6]*	∅1.4[7] ∅0.0224[8] ∅1.2[9] **∅3**				
	Batch-wise discharge [12]. Possibly as $Ca_3(SbO_4)_2$. Additive in plastics.							

	OPC (ppm)	Clinker (ppm)	CKD (ppm)	EPA (ppm)	C_3S (wt.%)	C_2S (wt.%)	C_3A (wt.%)	C_4AF (wt.%)
Se	<1-2.5[1] - [2]	**∅4**	∅17.5[6] ∅6.5[6] ∅18.3[6]	∅2.0[7] ∅8[9] **∅4**				
	Batch-wise discharge[12].							
Sn	<1-22[1] ∅4.6[1] **∅3**	**∅13**		<15[15] **∅10**				
	Low volatility.							
Te	<0.5[1] **∅5**	**∅5**		**∅1.4**				
Tl	0-2.68[2] *∅1.08*[2] 0-2[1] **∅0.6**	∅0.29[5] **∅0.5**	*∅43.24*[2]*∅17.1*[6] *∅4.62*[6] *∅88.0*[6] *∅40.6*[6]	300[15] ∅58[7] ∅71.7[8] **∅46**				
V	20-200[1] ∅56[1] **∅74**	∅56[5] **∅57**	*∅41.6*[6] ∅33.5[6]	25[15] ∅2456.6 [7] ∅3583.52 [8] **∅67**	0.5[20] 0.34[11]	1.3[20] 0.17[11]	0.1[20]	0.2[20]
Zn	20-400[1] ∅140[1] 6-657[23] ∅ 282[23] **∅164**	21-290[4] ∅96.4[5] laboratory: 4%[16],[17] **∅113**	*150*[2]*∅104.3*[6] *∅462*[6]	∅357.6[7] ∅362.42[8] ∅0.6-5[22] **∅91**	1.7[16] 0.65[20] 0.5[11] 5[13]	0[16] 0.2[20]	2[16] 0.4[20]	4.8[16] 1.2[20]
	In laboratory clinker as ZnO[16]. *Batch-wise discharge*[12].							

Table A12: Technical data and characteristic figures of kiln systems (typical ranges) [VDI 2094, 2003].

Kiln	**Rotary kiln** **with cyclone preheater**		**with grate preheater**
Capacity in t/d	3000 to 5000		300 to 3300
Heat consumption in kJ/kg clinker	3000 to 3800		3100 to 3800
Heat transfer equipment	Cyclone preheater		Grate preheater
Feed	Dry kiln feed		Granules (pellets)
Moisture content of preheater feed in vol. %	0,5 to 2,0*)		11 to 14
Exhaust gas upstream of dust collector	**with utilization of exhaust gas heat content in raw meal grinding unit**	**without utilization of exhaust gas heat content in raw meal grinding unit**	
Specific exhaust gas volume in m^3/kg clinker	2,1 to 3,0	1,7 to 2,2	1,8 to 14
Exhaust gas analysis in vol. % CO_2	14 to 22	20 to 35	20 to 29
Exhaust gas analysis in vol. % O_2	5 to 14**)	3 to 9	4 to 10
Exhaust gas analysis in vol. % CO	< 0,1	< 0,1	< 0,1
Exhaust gas temperature in °C	90 to 150	120 to 180	90 to 150
Water dew point in °C	45 to 60	50 to 65	50 to 65
Raw gas dust content (STP dry) in g/m^3	35 to 1000***)	20 to 100	2 to 14

*) for dry raw mix preparation process

**) with cooler exit air utilization up to 14 vol. %

***) higher raw gas dust content upstream of the dust collectors of the combined grinding and drying unit

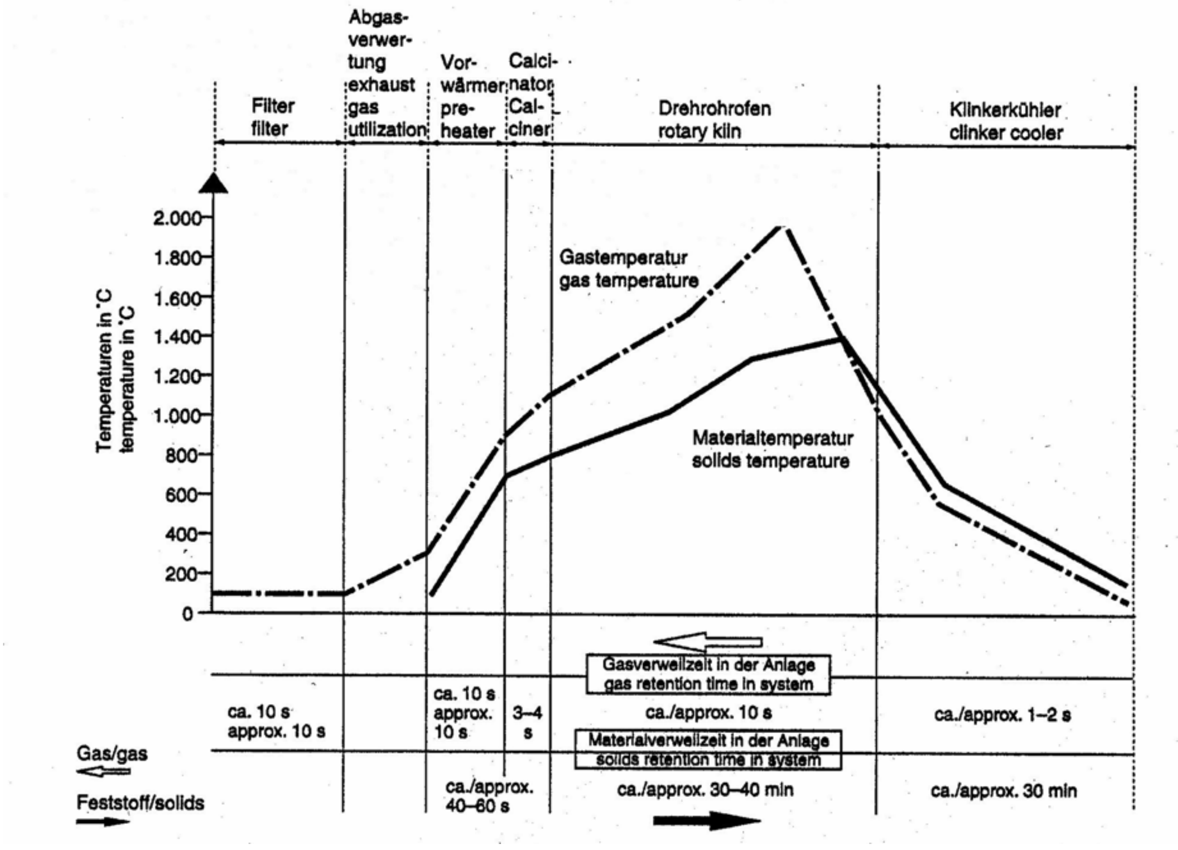

Figure A1: Gas and solids temperature profiles in a cyclone preheater kiln system [VDI 2094, 2003].