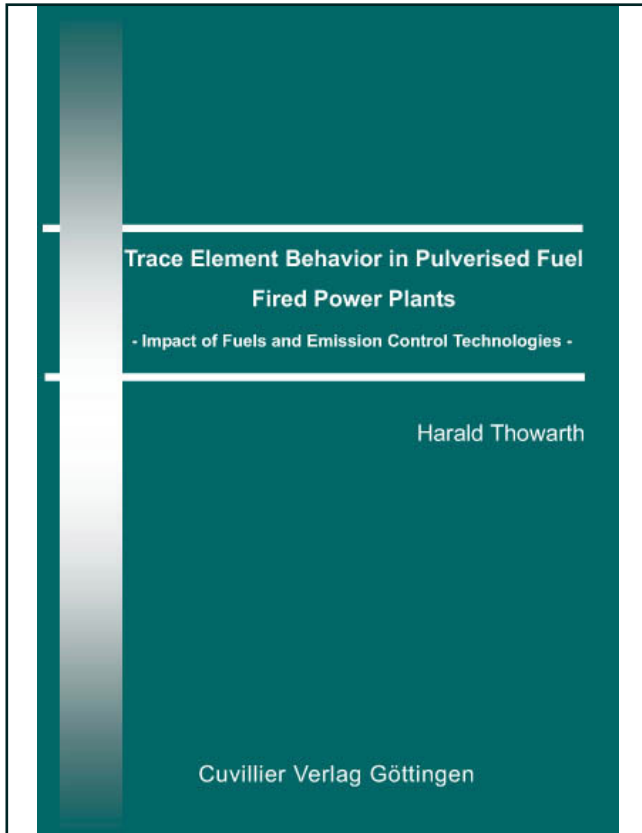




Harald Thorwarth (Autor)

Trace Element Behaviour in Pulverised Fuel Fired Power Plants

Impact of Fuels and Emission Control Technologies



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Telefon: +49 (0)551 54724-0, E-Mail: info@cuvillier.de, Website: <https://cuvillier.de>

1 Introduction

1.1 The Role of Coal-fired Boilers and their Emissions

The energy production within the European Union (EU) member states will increase between 2002 and 2030 by 52 % while the world wide increase will be even higher at 97 % [VGB 2006]. According to [VGB 2006], it is expected that the electricity demand in the EU 25 states will increase from today 3000 TWh to 4400 TWh per year in 2020. Due to the current average age of the power plants and due to the expected shut down of nuclear power plants in Germany, additionally about 1000 TWh of electricity production in Europe need to be replaced. Due to the fact that this gap cannot be filled with renewable fuels only, also in the future an energy mix will be necessary. Thus, in Europe as well as world wide, new coal-fired power plants are being built and additional capacity is expected to be installed.

Pollutants like nitrogen oxides (NO_x), particulate matter (PM) and sulphur dioxides (SO_x) are released at combustion processes. To remove particulate matter from the flue gas prior to emission, particulate control devices such as fabric filters and more important electrostatic precipitators are installed. Since NO_x and SO_x are harmful to the environment and human beings [BAUMBACH 1990], extensive research was done on those topics leading to convenient emission reduction technologies. Related to that, emission limits have been put in place. As a consequence, today all German coal-fired power plants are equipped with PM removal, DeNO_x and DeSO_x technologies and other European Countries and also the USA are following.

While in the past research was focused on the reduction of PM, NO_x and SO_x emissions, trace elements that are fed to the combustion process with the fuel, are of increasing concern, since they are harmful to the environment and the human body. According to the U.S. EPA it is likely, that mercury emissions affect the ecosystem. Furthermore, children who are exposed to relatively high levels of mercury before birth may be at increased risk of poor performance on neurobehavioral tasks, such as those measuring attention, fine motor function, language skill, visual-spatial abilities and verbal memory [WAYLAND 2005]. Since coal-fired power plants are identified to be one of the main sources of mercury emissions [MAYES 2005], legislative bodies are introducing emission limits for mercury but also for other trace elements. To meet those

limits, it is possible to install additional flue gas cleaning technologies like sorbent or oxidising agent injection systems as used in waste incineration plants. This first option causes additional investment as well as operating costs. Previous investigations showed, that DeNO_x, De-dust and DeSO_x technologies can have a positive effect on trace element emissions [MEIJ 1983]. The other option is therefore to use already available air pollution control devices like SCR-DeNO_x catalysts, electrostatic precipitators and flue gas desulphurisation (FGD) plants. This second option causes no additional costs. However, in order to reach a reliable trace element removal, detailed knowledge on the behaviour of trace elements in already applied air pollution control devices is necessary. Therefore mass balance studies were done at full scale power plants, reported e.g. in [MEIJ 1994], [FAHLKE 1994] and [MARTEL 2000], and particulate control devices and FGD systems were identified as main sinks. Following that, especially related to mercury behaviour, certain parameters were studied in more detail. In [HOCQUEL 2004] it is shown, that the application of SCR-DeNO_x catalysts enhances the removal of mercury in downstream wet FGDs under specific conditions. However, the mechanisms taking place and the parameters influencing the trace element sequestration in applied APCDs are yet not fully understood, which is necessary in order to reach better trace element separation efficiency.

It is known that carbon dioxide (CO₂) besides other pollutants contributes to the effect of global warming. The Kyoto Protocol demands the worldwide reduction of CO₂ emissions. However, the combustion of solid fossil fuels like lignite or bituminous coals causes CO₂ emission. So causes the power generation sector according to [IEA 2004] about one third of the total CO₂ emitted in the European Union. In general there are several ways to reduce CO₂ emissions in the power generation sector. Besides the application of carbon capture and storage (CCS) technologies, the combustion of CO₂-neutral biomass-fuels is one alternative option. This can be done in small dedicated biomass boilers or by co-firing biomass-fuels in large coal-fired utilities.

It is assumed, that co-combustion of biomass-fuels in coal-fired boilers does not only reduce CO₂ emissions, but it can also influence trace element behaviour during combustion and in the applied APCDs and subsequently the trace element emissions. Those fuels can contain higher or lower shares of trace elements than coals which cause the trace element input to be changed. Furthermore they also contain other constituents like e.g. chlorine in different concentrations as in coals. This can also influence trace element behaviour and therefore alter trace element emissions. However so far not many information about the influence of secondary biomass-fuels on trace element behaviour is available.

1.2 Objectives and Approach

The scope of this work is the investigation of the behaviour of trace elements in coal-fired power plants. The main objectives are to understand not only the impact of fire-side NO_x control

technologies but also SCR reactors as well as particulate control devices like electrostatic precipitators and fabric filter. In addition, the impact of the secondary biomass-fuels straw and municipal sewage sludge is investigated in detail. With an improved understanding of trace element behaviour along the flue gas path of coal-fired power plants it is aimed to be possibly able to reduce trace element emissions without the installation of additional and trace element specific flue gas cleaning technologies. In order to accomplish those objectives, the thesis is structured as discussed in the following.

In **chapter 2** basic information concerning the characteristics of trace elements are given. Based on literature data, the behaviour as well as the toxicity of chromium, copper, cobalt, nickel, arsenic, lead, cadmium and mercury is discussed, since those elements are studied in this work. The harmfulness of certain elements is furthermore linked to the development of legislations in Europe, Germany and the United States of America.

Chapter 3 introduces the area of trace element chemistry and the behaviour of trace elements in power plants. The origin of trace elements is discussed based on information given in open literature. In order to show differences between various coals and secondary biomass-fuels, trace element concentrations of different fuels are given. Furthermore, literature information on the behaviour of trace elements in coal-fired power plants and especially the influence of different air pollution control devices and other parameters are summarised.

Experiments are undertaken at two lab-scale and one pilot-scale test facility, applying various analytical methods. **Chapter 4** describes the experimental approach as well as the different measurement techniques used.

The subjects of matter of **chapter 5** are the results gained at the different laboratory-scale tests. In a first part the influence of certain metal oxides on mercury behaviour is studied. Therefore, different synthetic flue gases containing different components are used, while the metal oxides are investigated under fixed bed conditions. The purpose of these tests is to study the impact of individual metal oxides that can be contained in fly ash, on mercury oxidation, reduction and sorption at different temperatures and flue gas compositions. In the second part, another test facility is used to investigate the mercury behaviour in SCR-DeNO_x catalysts using again different synthetic flue gases in order to investigate the impact of different catalyst active components as well as catalyst operation conditions.

Chapter 6 describes the results of the pilot-scale investigations undertaken at a 500 kW_{th} pulverised coal combustion test facility equipped with a high dust SCR-DeNO_x catalyst, an electrostatic precipitator and a fabric filter. Tests investigating the behaviour and enrichment of trace elements in different fly ash fractions are carried out firing three different coals and co-

combusting biomass-fuels such as straw and municipal sewage sludge. Furthermore, the impact of applied air pollution control devices such as SCR catalyst, ESP and fabric filter is studied. Here, emphasis is laid on the impact of SCR operational conditions on mercury behaviour.

In **chapter 7** the results gained at the different test facilities are discussed evaluating also the comparability of lab-scale and the pilot-scale results and a possible transferability of the results to full-scale utilities.

The work is summarised in **chapter 8**, including conclusions as well as an outlook on future research needs in order to further improve the understanding of trace element behaviour in power plants and subsequently reach a continuing reduction of trace element emissions using already available air pollution control devices combined with advantageous fuel blends.

2 Trace Element Characteristics and Emission Legislation

This chapter gives basic information concerning definitions and characteristics of trace elements. Furthermore, properties, behaviour and especially the impact of trace elements on human health are discussed. Related to these informations the developments of trace element emission legislation for power plants are presented.

2.1 Characteristics of Trace Elements

2.1.1 Definitions

Elements present in coals in concentrations of 100 mg/kg and below are generally named trace elements (TE). Elements of the inorganic matter, such as Si, Al, Ca, Mg, K, Na, Fe, P and Ti, with concentrations in coal between 100 mg/kg and 10 g/kg are called minor elements and elements with higher concentrations that form the organic matrix of the coal, e.g. C, H, O, N and S are named major elements [GAUTHIER 2001], [ZEVENHOVEN 2001]. The majority of trace elements are also part of the heavy metals which are usually defined as elements with metallic attributes and a density of more than 5 mg/cm³ at a temperature of 300K [FAHLKE 1994]. As e.g. in [MARTEL 2000], arsenic is often also discussed as being a heavy metal even though it is a semimetal. Depending on the dose, heavy metals can be harmful to the human body and can lead to death; therefore they are often also called toxic metals. Toxicity was already discussed by Paracelsus: “Everything is toxic and nothing is without toxicity. Only the dose determines that a thing is toxic.” In the context of this study, the more general expression trace element is used.

2.1.2 Properties, Behaviour and Toxicity of Trace Elements

Trace elements, especially heavy metals are from a medical point of view of importance. Because the earth crust contains many of those elements, trace elements are in contrast to other toxic substances like dioxins natural components and it is thus not possible to remove them from the environment [DOTT 2002]. This means also, that there is a “natural background concentration” in the human body [NOWAK 2006]. Furthermore, some elements like chromium,

cobalt, copper, iron, manganese, molybdenum, selenium and zinc are discussed to be essential for the human body [DOTT 2002]. Since they are taken in with food in sufficient amounts, the toxic aspects are usually of greater importance [NOWAK 2006].

Trace elements are emitted to the atmosphere either from natural or anthropogenic sources. Natural sources are e.g. volcanism, soil erosion or aerosols originating from oceans [FAHLKE 1994]. Anthropogenic sources are the combustion of fossil- as well as waste- and biomass-fuels. Trace elements can also be emitted from industrial applications or products like chlorine – alkali electrolysis (mercury), electroplating (chromium), pigment colours (arsenic) or batteries (lead) [NOWAK 2006].

In the atmosphere, trace elements can travel long distances before they are deposited from air to surface water or soil either wet or particle bound. The residence time of trace elements in air increases generally with the volatility of the specific element [MERIAN 1984]. This means, due to the global air movements trace elements are not necessarily deposited close to the point of emission. So reports e.g. Brumsack in [BRUMSACK 1983], that due to the height of power plant chimneys the trace elements are not deposited close to the point of emission and Sullivan reports for the case of mercury in [SULLIVAN 2005] from a test campaign where it was not possible to correlate the mercury emissions of three power plants to the mercury depositions found close by those stations. This is also supported by EPA data given in [WEHRUM 2005] where it is stated, that 121 tons of mercury depositions in the United States out of a total number of 144 tonnes originate from emission sources outside of the USA and Canada.

There are different ways how trace elements can enter the human food chain respectively the human body. Figure 2-1 displays the most important ways of trace elements according to [UBA 1977] and [SRIVASTAVA 2005].

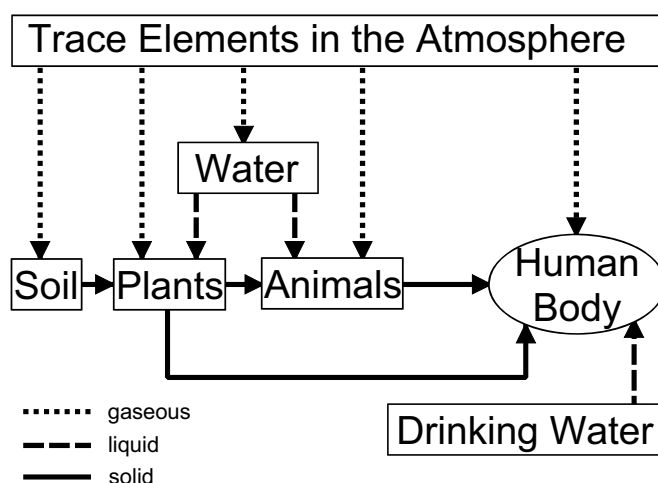


Figure 2-1: Trace elements in the human food chain, adapted from [UBA 1977] and [SRIVASTAVA 2005]

As seen in Figure 2-1, elements can enter the food chain via the soil, plants or animals or they can enter the human body directly via drinking water, breath or skin.

The toxicity of trace elements depends not only on the concentration but also on the electrochemical character and its solubility and furthermore on the oxidation state, e.g. arsenic(III)-oxide is more toxic than arsenic(V)-oxide [MERIAN 1984].

In this work the elements, chromium, copper, cobalt, nickel, arsenic, lead, cadmium and mercury are studied. Therefore more detailed information on those elements is given in the following.

Chromium

In case of chromium, the toxicity depends strongly on its oxidation state. Hexavalent chromium (Cr(VI)) is the toxicologically most relevant form of chromium which is mostly emitted from anthropogenic sources [DOTT 2002]. In the organism Cr(VI) is reduced to Cr(III). This means the Cr(VI) is a strong oxidising agent. This oxidising effect is the reason for the caustic effect on the skin and mucous membranes. Chromium furthermore damages the kidneys and causes lung cancer [BLEICH 2000].

Copper

Copper is known as a trace element which is essential for the human body. In case of copper the absorption and desorption is usually regulated by the body. However, for babies and young children, the increased absorption of copper due to significantly increased copper concentrations in the drinking water can cause cirrhosis of the liver [DOTT 2002].

Cobalt

Like other metals cobalt is known to be *in vitro* genotoxic. Furthermore, it is known to cause cancer [DOTT 2002]. Acute poisoning by ingestion causes gastro-intestinal reaction. Also inhalation of Co can result in sub-acute poisoning causing pulmonary system disorders and in long term leading to interstitial fibrosis and conjunctivitis. Some cobalt compounds are also suspected carcinogens [CIEPLIK 2005].

Nickel

The toxicity of nickel is strongly dependent on its chemical form [VDI 3956]. Volatile Ni complexes, are extremely toxic. Inhalation exposure to nickel compounds include acute pulmonary disorders (respiratory distress syndrome, which may even lead to death), as well as lung fibrosis, stomatitis and mucous membranes destruction due to chronic exposure [CIEPLIK 2005].

Arsenic

The absorption of arsenic takes place mostly via inhalation. However, significant amounts of arsenic can also be absorbed via the skin [BLEICH 2000]. The inhalation causes a caustic effect at skin and mucous membranes. The absorption can also cause lung cancer as well as skin tumours [NOWAK 2006].

Lead

The absorption of lead can take place either via the respiratory system as well as via the skin. The most important toxic effect of lead is a damage of the central nervous system, causing depressions and other psychological changes. In addition, lead can also damage the kidneys [BLEICH 2000].

Cadmium

The inhalation of cadmium causes an irritation of the respiratory tract and lung oedema [NOWAK 2006]. Oral absorption of cadmium can also damage the kidneys and it is furthermore known as carcinogen [BLEICH 2000].

Mercury

Mercury is mostly absorbed via the lungs. Up to 80% of the inhaled mercury reaches the blood [BLEICH 2000]. Acute mercury poisoning causes irritations resulting in tracheobronchitis and damage of the central nervous system. Chronic mercury poisoning damages the kidneys and the central nervous system. Women of childbearing age are regarded as the population of greatest concerns, because the developing foetus is most sensitive to the toxic effects of methylmercury. According to US EPA children who are exposed to relatively high levels of mercury before birth may be at increased risk of poor performance on neurobehavioral tasks, such as those measuring attention, fine motor function, language skill, visual-spatial abilities and verbal memory [WAYLAND 2005].

2.2 Development of Legislations

As discussed above, trace elements are emitted from various sources and distributed in the atmosphere, before they are deposited and enriched in soil or water. In this way trace elements and especially mercury can reach the human body as discussed in chapter 2.1.2. Since they can be harmful to human beings there are trace element emission limits for industrial combustion systems in place. In the following subchapters current trace element emission limits for fossil fuelled power plants in Europe, Germany and the United States of America are discussed. Since mercury is the most important trace element, it is also the most limited element. The development of mercury emission limits is discussed also to give possible trends for the future.

The trace element emission limits presently in place originate from the 1970s. There, it was seen that sulphur emissions in central Europe can cause an acidification of lakes in Scandinavia. This led to the “**Convention on Long – range Transboundary Air Pollution**” [UN-ECE 1979], which was signed by the European Community and 34 other countries including Germany and the United States of America. Since that the convention was extended by eight further protocols. One of these protocols is the “**Protocol on Heavy Metals**” [UN-ECE 1998], which was signed in 1998. Here the elements cadmium, lead and mercury were identified as especially dangerous metals. One of the basic commitments of the signing countries was to reduce the emissions of those three metals below the level of 1990. The goal of this protocol was to reduce the emissions of technical combustion processes.

2.2.1 Legislation in Europe

The next step in Europe was the “**EU-Directive 2001/80/EC**” (Large Combustion Plant Directive) [EC 2001-1] on the limitation of emissions of certain pollutants into the air from large combustion plants. This document recommends, based on the Convention on Long-range Transboundary Pollutants, the adoption of measures to reduce heavy metals emitted by certain installations. Since particulate control devices do not only reduce the particulate emissions but also the emissions of particle bound trace elements, the employment of such facilities was recommended. However, there are no trace element emission limits set.

The publisher house of the European Union published in October 2001 a “**Position Paper on Ambient Air Pollution by Mercury**” [EC 2001-2]. This document was prepared by a working group on mercury and gives an overview on the problems related to mercury emitted from natural and anthropogenic sources as well as on possibilities for a reduction of the emissions.

The council of the European Union asked the EU Commission in December 2002 to prepare an EU strategy for mercury and to present it in 2004. The Directorate-General (DG) Environment published in March 2004 a “**Consultation Document**” [EC 2004] asking all parties interested in preparation of an EU strategy on mercury for consultation.

The Commission of the European Communities presented then in January 2005 an “**EU Strategy on Mercury**” [EC 2005] where the key aim is to reduce mercury levels in the environment and human exposure. In this document coal burning is identified as one of the main sources of mercury releases. Based on the EU strategy on Mercury further decisions on mercury emission limits are expected.