

**Leaching of fly ash particulate matter in MEA solutions  
and its relevance to the CO<sub>2</sub> capture process  
with flue gas of coal-fired power plants**

Die Auslaugung von Flugasche in MEA Lösungen  
und ihre Bedeutung für die großtechnische Abscheidung von CO<sub>2</sub>  
aus dem Rauchgas Kohle-gefeuerter Kraftwerke

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# List of abbreviations, symbols, and indices

## Abbreviations

av.	average value
CaO <sub>free</sub>	free lime
HOH <sub>2</sub> C-CH <sub>2</sub> NHCOO <sup>-</sup>	mono ethanolamine carbamate ion
CC	carbon capture
H <sub>3</sub> C-COOH	acetic acid
CO <sub>2</sub>	carbon dioxide
CO <sub>3</sub> <sup>2-</sup>	carbonate ion
HOOC-COOH	oxalic acid
demin	demineralized water
EDTA	ethylenediaminetetraacetic acid
ESP	electrostatic precipitator
ettringite	Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O
FF	fabric filter
FGD	flue gas desulfurization
FTIR	Fourier transform infrared spectroscopy
GGH	gas-gas heater
HOH <sub>2</sub> C-COOH	glycolic acid
HCO <sub>3</sub> <sup>-</sup>	hydrogencarbonate ion
HEF	N-(2-hydroxyethyl) formamide
HEGly	N-(2-hydroxyethyl) glycine
HSS	heat stable salt
HPO <sub>4</sub> <sup>2-</sup>	hydrogenphosphate ion
IC	ion chromatography
ICP-OES	inductively coupled plasma optical emission spectroscopy
LOD	limit of detection
MEA	mono ethanolamine
MEAH <sup>+</sup>	protonated mono ethanolamine molecule

meq	milliequivalent
nld	non-loaded
NH <sub>3</sub>	ammonia
NH <sub>4</sub> HSO <sub>4</sub>	ammonium hydrogen sulfate
NO <sub>x</sub>	sum of NO and NO <sub>2</sub> , calculated as NO <sub>2</sub>
PP	power plant
PSD	particle size distribution
RPM	revolutions per minute
SCR	selective catalytic reduction of nitrogen oxides
sEF	specific enrichment factor, flue gas flow per liquid inventory
SEM	scanning electron microscope
SO <sub>2</sub>	sulfur dioxide
std.	standard deviation according to n-1
vc	variation coefficient
XRF	x-ray fluorescence spectroscopy

### **Symbols**

M	molar, mol/kg
STP	standard condition at 0 °C and 1013.25 mbar
n	number of elements considered for the statistical evaluation

### **Indices**

el	electric
free	free lime or free magnesium oxide
inv	liquid inventory of the CC plant
tot	total amount of e.g. CaO

# Abstract

During the CO<sub>2</sub> carbon capture (CC) operation in coal-fired power plants (PP), particulate matter accumulates over time and undergoes leaching in mono ethanolamine (MEA) solutions. Previous studies usually assessed only one sample of fly ash, collected from the electrostatic precipitator (ESP) of a given PP, and they differed in terms of the leaching parameters and the scope of analysis. The present study underlines the relevance of leaching to CC plants and strives for a better understanding of the solubility of various elements and heavy metals, especially Fe, in MEA solutions and of relevant leaching parameters.

Using parallel tests, this study assesses the leaching of ESP ashes from three PP in a rich loaded 5 M MEA solution under various conditions, resulting in a comprehensive dataset on five physical parameters, five macro elements and six heavy metals within each of 30 leachates.

The remaining study describes measurements with three solid to liquid ratios using a lean 5 M MEA and two new ESP ashes to assure the repeatability of the whole procedure (leaching and analytics) by four repetitions for each ESP ash and solid to liquid ratio. These analytical results are used to forecast the Fe concentration for the early beginning of a CC plant.

The main results are summarized as follows:

- The rich loaded 5 M MEA solution dissolves an enormous amount of Fe compared to pure water. Each ESP ash dissolves Fe and the other heavy metals specifically.
- The Fe concentration increases disproportionately with increasing molar concentration of the rich loaded MEA solution.
- The glycolate concentration as a degradation product enhances predominantly the dissolution of Fe at the high concentration of 50 mmol/l. The oxalate concentration may suppress the Fe concentration by precipitation.
- With lower solid to liquid ratio the concentration of all analysed elements and compounds decreases, but specifically for each element/compound and ESP ash when solid concentrations of several g/kg occur.
- For ratios < 1:1000 (g/g) the dissolved concentrations for different ESP ashes become quite similar and the specific character of each ESP ash becomes less important.
- The repeatability values point out variation coefficients predominantly below 5 % for Mg, Ca, S, Fe, V, Cr and Mn.



- The leachate results at 1:1000 (g/g) for one ESP ash are used for further extrapolation to the start of CC operation.
- Apart from main elements such as Ca, Mg and S, only Fe is forecasted to be detected in the lean 5 M MEA solution of a CC plant after 24 h of operation, when 1 mg /m<sup>3</sup> of fly ash is absorbed by the circulating liquid and an enrichment factor of 0.8 m<sup>3</sup>/(I<sub>inv</sub>\*h) is applied.

To optimize the performance of a CC plant the inlet fly dust concentrations (50 % fly ash assumed) are recommended to be lower than 0.6 mg/m<sup>3</sup> (STP, dry, 6 % O<sub>2</sub>) to control the accumulated fly ash below 1 g/kg for at least 4000 hours, when an enrichment factor of 0.8 m<sup>3</sup>/(I<sub>inv</sub>\*h) is applied.

# Kurzfassung

Flugstaubkonzentrationen werden mit dem Rauchgas in die Carbon Capture (CC)-Anlage eines Kohlekraftwerks eingetragen. Absorbierter Flugstaub wird mit der Betriebszeit angereichert und unterliegt Lösungsvorgängen in Monoethanolamin-Lösungen (MEA). Bisherige Untersuchungen mit Elektrofilteraschen sind überwiegend Probe für Probe untersucht und nicht immer mit den gleichen Auslaugungsparameter durchgeführt worden. Auch bestanden Unterschiede im Analysenaufwand für die Schwermetalle. Diese Studie unterstreicht mit den Ergebnissen zur Auslaugung von Hauptbestandteilen und Schwermetallen, vor allem von Eisen, aus Elektrofilteraschen die Bedeutung für den CC-Betrieb mit MEA, betont die wichtigen Auslaugungsparameter und schafft damit ein besseres Verständnis für die in einer CC-Anlage ablaufende Auslaugung mit Flugstaub.

Diese Arbeit befasst sich mit parallel durchgeführten Elutionen an drei unterschiedlichen Elektrofilteraschen unter den wichtigsten Auslaugungsbedingungen, wobei immer dieselbe mit CO<sub>2</sub> beladene, 5 molare MEA-Lösung eingesetzt wurde. Der umfangreiche Datensatz enthält für jedes der 30 Eluate die Ergebnisse von 5 physikalischen Summenwerten, 5 Makroelementen und 6 Schwermetallen.

Die verbleibende Studie behandelt Untersuchungen an zwei weiteren Elektrofilteraschen bei drei Verhältnissen von Feststoff zu Flüssigkeit mit einer CO<sub>2</sub> teilbeladenen, 5 molaren MEA-Lösung, um über vierfache Wiederholungen der Auslaugung und Analytik die Ergebnisse abzusichern. Analyseergebnisse dieser Untersuchung sind Basis für eine Abschätzung der Fe-Konzentration zu Betriebsbeginn einer CC-Anlage.

Die wesentlichen Ergebnisse lassen sich wie folgt zusammenfassen:

- Die mit CO<sub>2</sub> beladene, 5 molare MEA-Lösung hält große Konzentrationen an Fe nach der Auslaugung von E-Filterasche in Lösung, sehr viel mehr als vollentsalztes Wasser. Die Konzentrationen von Fe und den anderen Schwermetallen verhalten sich E-Filteraschen-spezifisch.
- Die Zunahme der Fe-Konzentrationen im Eluat mit steigender Molarität der mit CO<sub>2</sub> beladenen MEA-Lösung ist überproportional.
- Glykolat als Alterungsprodukt erhöht die Auslaugung von Fe aus E-Filteraschen. Oxalat kann die Löslichkeit von Fe durch Fällung herabsetzen.

- Mit abnehmendem Verhältnis von Feststoff zu Flüssigkeit sinken die nachweisbaren Element-Konzentrationen. Das Verhalten im g/l-Bereich (Feststoff zu Flüssigkeit) ist Element- beziehungsweise Verbindungs-spezifisch und charakteristisch für jede E-Filterasche.
- Ab 1:1000 (g/g) sind diese Unterschiede klein und die Eluate der verschiedenen E-Filteraschen gleichen sich immer mehr an.
- Die Ergebnisse der Reproduzierbarkeitsmessungen weisen für Mg, Ca, S, Fe, V, Cr und Mn Variationskoeffizienten überwiegend kleiner 5 % aus.
- Die Messergebnisse für das Eluat einer E-Filterasche bei einem Verhältnis von 1:1000 (g/g) sind für die Modellrechnungen zu den erwarteten Konzentrationen zu Betriebsbeginn einer CC-Anlage genutzt worden.
- Wenn 1 mg/m<sup>3</sup> Flugstaub in einer CC-Anlage absorbiert werden und ein spezifischer Anreicherungsfaktor von 0,8 m<sup>3</sup>/(l<sub>inv</sub>\*h) besteht, sind abgeschätzt bereits 24 Stunden nach der Inbetriebnahme der CC-Anlage geringe Konzentrationen an Mg, Ca, S und Fe in µg/l in der mit CO<sub>2</sub> teilweise beladenen MEA-Lösung aufgrund der Auslaugung des Flugstaubes nachweisbar.

Um eine Betriebszeit von zumindest 4000 Stunden mit Staubkonzentrationen kleiner 1 g/kg zu erreichen, sollte die Konzentration an Flugstaub (davon 50 % Flugasche) im Rauchgas vor dem Absorber der CC-Anlage 0,6 mg/m<sup>3</sup> (STP, dry, 6 % O<sub>2</sub>) bei einem Anreicherungsfaktor von 0,8 m<sup>3</sup>/(l<sub>inv</sub>\*h) nicht überschreiten.

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# 1 Introduction

## 1.1 Initial situation

Scrubbing out CO<sub>2</sub> from fossil fuel related flue gases and avoiding emissions requires a reliable technique for the absorption of CO<sub>2</sub> and, of course, the storage or the reuse of the absorbed CO<sub>2</sub> quantities. Publically funded research projects since 2004 like CASTOR [Knudsen 2008], CESAR [Knudsen 2011], Cato [Goetheer 2009], OCTAVIUS [Rieder 2016] or COORETEC ([Jockenhoevel 2009] and [Schäffer 2013]) and later research investigations by the power industry and engineering companies [Huang 2010], [Moser 2011], [de Koeijer 2011], [Medjell 2011], [Rieder 2013], [Reddy 2013], [Radgen 2014], [Wieclaw-Solny 2014], [Fitzgerald 2014], [Gorset 2014], [Brigman 2014], [Dux 2016], [Rieder 2016] and [Knudsen 2017] mainly focused on liquid absorption/desorption processes using alkanol amines in water. These projects, which included the operation of pilot plants, collected experiences regarding the energy demands for absorption and stripping, degradation of solvents, formation of heat stable salts, reclaiming tests [Rieder 2016], emission of solvent related compounds such as ammonia, aldehydes and nitrosamines [Fraboulet 2016], and the enhanced emissions of solvent species based on aerosols [Khakharia 2013] which could be a minor part of the flue gases entering the carbon capture (CC) plant.

All these above cited pilot plants have in common that the time of operation was quite short compared to a commercial plant (less than 4000 hours before the complete replacement of solvent inventory). In addition, heavy metal concentrations such as mainly iron as well as sometimes chromium, nickel and molybdenum increased over time to varying degrees in different pilot plants, but most likely catalysing the oxidative degradation of the solvent as studied by laboratory tests [Chi 2000, Goff 2005, and Sexton 2008] and leading to enhanced demands of the solvent material and increased emissions of especially ammonia [Rieder 2016].

The sources of iron and, to a lower extent, of the other heavy metals like chromium, nickel and molybdenum have not been intensively studied or are not yet published. Based on studies with the accumulated heavy metal concentrations and the metal surface areas at the rich/lean heat exchanger, which consists of stainless steel, [Unterberger 2013] found that corrosion

occurs under lean and hot conditions. Generally summarized, if we exclude mistakes during the construction of the pilot plant due to wrong materials, the presence of iron and other heavy metals can presumably be attributed to the following sources:

- The welding of the stainless steel material might be insufficient ,
- the used stainless steel material is not been completely covered by a stable chromium oxide layer,
- the used stainless steel material undergoes corrosion reactions within certain parts of the process because of the liquid properties,
- **and/or** there is an intake of iron and other heavy metals due to the process.

Flue gases from coal-fired power stations contain particulate matter at the emission point depending on the ash content of the fuel and the efficiency of the installed flue gas cleaning devices. More than 99.9 % of the fly ash concentration in the flue gas at the boiler end are typically rejected within an electrostatic precipitator (ESP) which is the mostly used cleaning device for fly ash. A further reduction takes place within the flue gas desulfurisation plant (FGD). The flue gas downstream FGD will be the feed gas for a CC plant. Quite small amounts of particulate matter will enter the CC plant, will be absorbed and will accumulate over time in the absorbing liquid. Depending on the composition of the particulate matter at the surface layer of the particles and their solubility in the solvent according to the liquid temperature and composition, leaching will take place. Iron is a main compound of the fly ash particulate matter, thus dissolved iron concentrations might occur with increasing operation time due to absorbed and leached fly ash particulate matter, even if there is no corrosion at all.

Parallel to the accumulation and leaching of fly ash particulate matter, degradation products of the alkaline amine solution are formed and also accumulate over time. The rate of the formation differs from pilot to pilot plant. Such degradation products are for instance carbonic acids formed by oxidation reactions and neutralized by the alkaline amine to dissolved salts. The impact of carbonic acids as degradation products on enhanced leaching of rejected fly ash particles can be expected, but has not been completely studied in laboratory leaching tests as a function of the concentration and in mixtures for the carbonic acids concerned.

This study focuses on the role of absorbed fly ash particulate matter in CO<sub>2</sub> loaded MEA (mono ethanolamine) solutions and its impacts due to the leaching of particulate matter. ESP ash samples are used to demonstrate the leaching for the heavy metals of interest. MEA solution, mainly 5 molar (M), constitutes the absorbing liquid that has been used in each pilot plant as

a “standard” liquid, at least at the beginning, in order to identify the starting level for any improvement of performance and to verify the properties of other solvents.

## 1.2 Objectives and approach

This study contributes to a better understanding of the leaching of fly ash particulate matter after the absorption into the MEA solution and provides recommendations regarding an improved performance of CC plants using MEA solution for absorption. The underlying objectives are:

- To point out which heavy metals are leached from ESP ashes of three different hard coal-fired power stations (spot samples) by rich loaded 5 M MEA,
- to determine the relevant parameters that support the leaching of these heavy metals from the three different ESP ashes using the same leaching solution in parallel tests,
- to reproduce four times the results in additional measurements with two ESP ash samples for three solid to liquid ratios of 1:100 (10 g/kg), 1:1000 (1 g/kg) and 1:10000 (100 mg/kg), using lean 5 M MEA at room temperature over 24 hours, to assure the whole procedure of leaching and analytics,
- to forecast the heavy metal concentrations of leached fly ash as a function of the operational time for a defined commercial CC plant, and
- to draw conclusions from these results and propose countermeasures for a better performance of CC plants.

In order to accomplish these objectives, the approach is as follows:

**Chapter 2** contains the literature survey and describes the state of knowledge.

**Chapter 3** describes the materials and methods, including the sampling of the ESP ashes, the properties of the liquids used for the leaching, the procedure to produce the leachate, the applied instrumentation, the analytical tools and the experiments.

**Chapter 4** documents the experimental results, including lessons learned at the end of each part.

**Chapter 5** discusses the results, in particular the behaviour of Fe and the related parameters. Interpretations of certain results, comparisons to published data, and proposals for future work are included.

**Chapter 6** summarizes the results, draws conclusions, and provides recommendations for the planning and operation of a commercial CC plant.

## 2 State of knowledge

Two materials are involved in this study, a liquid and a solid. The liquid consists of 70 % demineralized water and of 30 % mono ethanolamine, called a 5 M MEA solution. The 5 M MEA solution is usually used as the absorbing liquid in a cyclical process at the end of a pipe of the flue gas cleaning in coal-fired power plants. As for the solid material, this study deals with fly ash produced by the milling and the burning of coal. Each coal possesses a certain amount of ash which cannot be avoided at all, only reduced by coal treatment. The disposal or the re-use of the rejected fly ash mass has been an issue from the beginning when electricity production started based on the combustion of coal.

Understanding the interaction of those two materials in the context of carbon capture in coal-fired power plants requires a few preliminary remarks on the production of fly ash and the process of carbon capture.

In Germany, the production of fly ash usually takes place in dry bottom boilers, which have been used for roughly 30 years in large power plants (> 300 MW<sub>el</sub>) and are also the most common ones worldwide. Coal is pulverized in mills and blown into the furnace with the air as a carrier and as a supplier of oxygen for a nearly complete burning of the coal particles. The quality of the grinded coal is important for the efficiency of the electricity production and the contamination of the fly ash by unburnt carbon particles. The fineness of the grinded coal at the outlet of the mills has to fulfil a distinct particle size distribution in order to keep the content of unburnt carbon concentration below 4 % in the rejected fly ash. Most of the grinded coal particles have grain sizes below 90 µm. How much residue on a 90 µm sieve can be accepted by the operator, depends on the coal parameters such as grindability and content of volatiles and on the technical aspects of the furnace itself. In any case, deriving from a fine grinded coal an even finer fly ash is the result of combustion. Most of these fly ash particles (85-90 %) are transported by the flue gas through the boiler and must be captured either by an ESP or a fabric filter (FF). Inside the furnace 10-15 % are agglomerated to bigger particles, called coarse ash, and fall down by weight into a cooled water bath underneath the furnace. The mean temperature inside a dry bottom furnace is typically around 1400 °C. The residence time of the particulate matter inside the furnace is sufficient

- to melt nearly each ash particle and produce more or less molten bowls, which shortly after leaving the furnace harden into glass balls,
- to vaporize elements such as Hg and Se and to form chemically compounds such as SO<sub>2</sub>, HCl, HF and NO<sub>x</sub> in the flue gas which have to be taken out by cleaning devices, and
- to release as well inside the furnace gaseous traces from the coal or the ash to the flue gas like some heavy metals e.g. Cd, Pb, Tl or other elements like Na, K, As, Sb in elementary form or as oxides or as chlorides which condensate at the surface of the fly ash particles again during the flue gas pathway through the boiler, specifically for each compound depending on the saturation temperature.

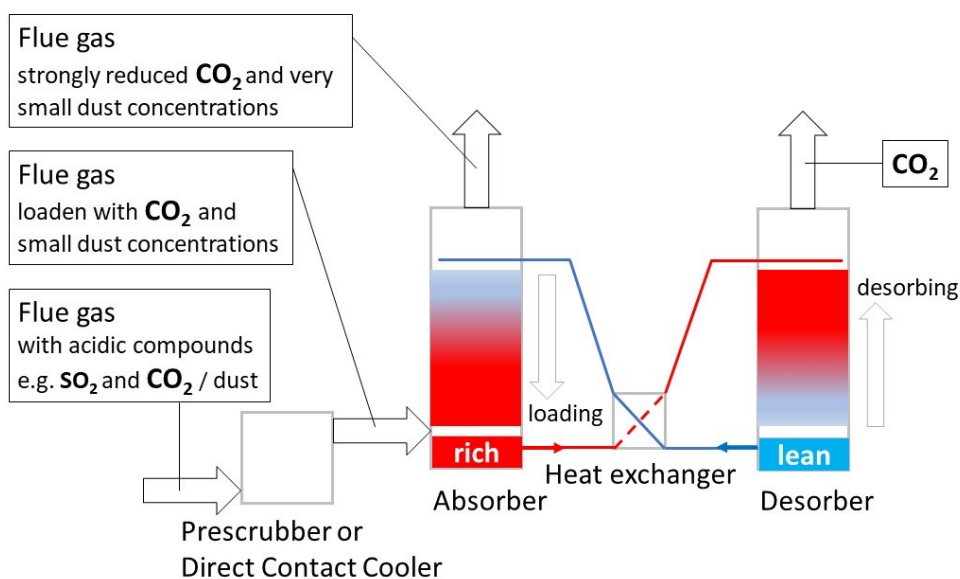
Considering the particle size distribution of the fly ash, those elements or compounds, which are vaporized inside the furnace, are enriched on small particle sizes. If all ESP stages are separately sampled and analysed, then an enrichment of e.g. some heavy metals is recognized for the last ESP stage. This is also the reason for a shift in the composition for some elements when compositions of coarse ash, rejected fly ash from an ESP and emitted fly ash particulate matter, parallel sampled and dried, are compared.

Condensed material at the surface of the particles is, of course, at first accessible for any reaction which might occur. This concerns firstly all emission and deposition aspects, but secondly as well the re-use of fly ash material and thirdly the leaching of disposed fly ash which might influence to the composition of soil and groundwater.

Leaching test standards have been applied in order to evaluate the properties of fly ash material regarding the behaviour when wetted. Anderson [Anderson 1979] and Ham [Ham 1980] developed the rules for a leaching standard test which in 1984 became a German standard [DIN 38414 1984] and in 2003 a European standard [EN 12457-4 2003-01].

During carbon capture in coal-fired power plants, CO<sub>2</sub> is washed out from the flue gas in an absorber column. The flow of the flue gas is upwards whereas the liquid rinses down at the surfaces of e.g. structured packings, increasing the load of CO<sub>2</sub> in the liquid to the maximum level, which is called rich solution (Figure 1). From the bottom of this column the rich solution is pumped through a cross-rich/lean-heat exchanger to a stripper column where CO<sub>2</sub> is stripped out by steam, as well in a counter current flow. From the bottom of the stripper column the partly CO<sub>2</sub> desorbed liquid, called lean solution, is pumped back through the mentioned heat exchanger to the absorber column, homogeneously distributed on top of the

structured packings of the absorber, to close the circuit. To install a prescrubber or a direct contact cooler upstream the CC absorber (Figure 1) is advantageous because small amounts of acidic compounds in the flue gas e.g.  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{HCl}$  can be washed out in order to avoid the formation of heat stable salts (HSS) in the MEA solution. Detailed information about the technical aspects of the carbon capture by alkanol amines as well for MEA is given by [Kohl 1997]. [Feron 2016] published the status quo of carbon capture from fossil fuel flue gases. Within this process, MEA solutions play a central role because it is an alkanol amine which is used in small commercial industrial plants since several years and a lot of experience is available. This liquid is a cheap base chemical. As an absorbing liquid for flue gas from coal-fired PPs, it undergoes oxidative degradation by the  $\text{O}_2$  of the flue gas and is probably affected by heavy metals leached from absorbed fly dust particles. The leaching of rejected particulate can be one source of Fe in the MEA solution.



**Figure 1:** Schematic diagram of a MEA based CC plant of a coal-fired PP

Although oxygen of the flue gas is absorbed to a very low extent depending on the liquid temperature, oxidative degradation of MEA occurs over time. When Fe, Cu, Cr, Ni or V are dissolved into the loaded MEA solution, then the oxidative degradation is intensively accelerated by the catalytic support of these heavy metals [Chi 2000, Goff 2005, Sexton 2008]. This enhanced oxidative degradation by catalytic support is problematic because of increased



ammonia ( $\text{NH}_3$ ) emission and higher losses of MEA. That is why corrosion of steel should be avoided at all and the intake of Fe etc. should be at a minimum.

The remaining chapter summarizes our current understanding regarding different aspects of ESP ash properties, the impact of ESP ashes on MEA solutions, and the properties of fly dust after wet desulfurization plants.

## 2.1 ESP ash properties and leaching by demineralized water

The ESP ash from hard coal-fired power plants is a heterogeneous material due to the particle size distribution and differences in the composition of these particles [Smith 1980]. There are predominantly coal ash particles with varying compositions. Less frequently, limestone ash particles, called free lime, and unburnt carbon particles exist.

[Kutchko 2006] described how mineral matter in coal transforms into fly ash particles during combustion and provided a good survey about the morphology and the chemical characterization of selected fly ash particles.

[Richartz 1975] analysed 30 ESP ashes from German hard coal-fired power stations in terms of the grain size distribution and the composition. The bandwidth in the grain size distribution ranged from  $8\ \mu\text{m}$  to  $50\ \mu\text{m}$  for 50 % of the particulate mass with an average of  $32\ \mu\text{m}$ . These fly ash particles were predominantly glass spheres. The bandwidth of free lime ( $\text{CaO}_{\text{free}}$ ), which depends on the total CaO content ( $\text{CaO}_{\text{tot}}$ ), varied between 0 %  $\text{CaO}_{\text{free}}$  (0.53 %  $\text{CaO}_{\text{tot}}$ ) and 1.63 %  $\text{CaO}_{\text{free}}$  (10.2 %  $\text{CaO}_{\text{tot}}$ ) with an average value of 0.25 %  $\text{CaO}_{\text{free}}$  (3.84 %  $\text{CaO}_{\text{tot}}$ ). Crystalline material such as quartz ( $\text{SiO}_2$ ), mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), and magnetite ( $\text{Fe}_3\text{O}_4$ ) was also found mainly inside the fly ash spheres. A significant part of the fly ash particles was hollow, called cenospheres.

[Raask 1985] and [Neto 2016] provided additional information about the formation of cenospheres.

Kautz [Kautz 1986] evaluated the dependency of the free lime content of ESP ashes from the total amount of CaO for coals from different regions in Germany. Free lime in rejected fly ash mainly occurs when the total amount of CaO is above 2.0 %. Additionally, [Kautz 1986] determined the particle size distribution and documented the morphology of the particulate matter by photos from a scanning electron microscope (SEM) which visualizes condensed

material at the surface of fly ash particles, quite distinct for the ESP ashes from different boilers.

[Fisher 1979] clearly stated that the most soluble part of fly ash particulate matter derives from the surface layer, which is rich in trace elements. He published a list of elements that are leached from a typical coal fly ash, while emphasizing that the cations and anions present in the solution can interact. Multiple equilibria might occur involving e.g. complexation and precipitation.

[Wilberley 1982] and [Iyer 2002] pointed out that the surface layer on the top of fly ash particles contains leachable material that is deposited along the flue gas pathway due to cooling. This layer is exceptionally thin (approximately parts of microns). In water 1-3 % of the fly ash material is soluble. Iyer concluded that the particle size distribution of the fly ash material from a lignite coal combustion is not changed by the leaching process. No results are published for ESP ashes from hard coal-fired power plants according to the particle size distribution of the material after leaching.

Elseewi et al. [Elseewi 1980] determined the chemical composition, pH and conductivity of the leachates produced by an US western coal fly ash with demineralized water at room temperature, over 24 hours and for varying solid to liquid ratios of 1:5, 1:10, 1:20, 1:40, 1:80, 1:250, 1:500 and 1:1000 (g/g). He confirmed that the measured conductivity values are proportional to the sum of dissolved elements and compounds in solution, calculated as milliequivalent per l. Due to the complex matrix of the fly ash, Elseewi et al. doubt whether a true equilibrium exists for any particular dissolved constituent.

The monography by [Tauber 1988] summarizes the knowledge about the behaviour of trace elements in fly ash up until the late 1980s. Chapter 3.3, p. 164-181, deals with leaching tests under laboratory scale and lists the main parameters for leaching of fly ashes with demineralized water that affect the leachate quality. These parameters include the composition of the fly ash, the condensed material at the surface of the particles, the grain size distribution, the liquid to solid ratio, the time for leaching and the temperature. For landfilling, of course, the pH-value has to be considered, for closed systems this value results from the composition of the fly ash.

[Querol 2000] analysed and leached 12 ESP ashes from hard coal-fired Spanish power stations (all dry bottom boilers, but not yet retrofitted by SCR (selective catalytic reduction of NO<sub>x</sub>) and FGD (flue gas desulfurization) cleaning devices) plus one from China and one from a fluidized-

bed combustion, using a solid to liquid ratio of 1:50 (ESP ash to demineralized water, g/g), 24 hours leaching time, room temperature, and a stirring technique. The leachate quality was continuously controlled by conductivity and pH measurements. Within the first five minutes of leaching the pH of 11 different ESP ashes increased from neutral to levels between pH 9.5 and 12.5 with a very low further increase by time. Only one ESP ash showed an acid drop at the beginning (to pH 4.6) and then an increase to a pH of 8. The reason of this quite different behaviour results from the ratio Ca to S (meq/meq). A high surplus of Ca by free lime shifts the pH to higher values, but near to 1 and especially below 1, the pH value drops depending on the surplus of S. The concentration values of 32 elements (macroscopic ones like Ca and S, but as well heavy metals like Fe and Cr) are listed for the leachate quality. The results as average values are for Fe 0.16 mg/l, for Cr 0.05 mg/l, for Ni 0.006 mg/l, for V 0.11 mg/l, for Cu 0.002 mg/l, and for Mo 0.07 mg/l under those leaching conditions (1:50 (g/g), room temperature and 24 hours).

An even wider study has been published by Moreno et al. [Moreno 2005] who included 22 ESP ashes from European hard coal-fired power stations plus one lignite-fired one. This examination covers chemical, mineralogical, physical, and glass characterization, but as well leaching tests at room temperature for 24 hours with a solid to liquid ratio of 1:10 (g/g) according to [EN 12457-4]. Analytical data of the leachates are presented for pH, conductivity, and 39 elements. The average concentration for Fe is 0.14 mg/l with a high variation coefficient of 161 %. Six of 22 Fe results are above 0.2 mg/l with a maximum of 0.98 mg/l, but 16 results are below 0.11 mg/l. The average values for Cr are 0.27 mg/l, for Ni 0.02 mg/l, for Mo 0.37 mg/l, and for V 0.12 mg/l. There seems to be no correlation between the Fe content in the ESP ash and the Fe concentration in the leachate.

[Gitari 2009] determined the leaching behaviour of two ESP ashes from South African hard coal-fired power plants using demineralized water under [DIN EN ISO 11885, 1:10 (g/g), 24 h, 22 °C] conditions. With pH values above 12 at the end of the leaching time, the concentration of Fe was around 9 µg/l, whereas the V, Mn, Ni and Cu concentrations were below the limit of detection. The value for Cr was around 359 µg/l. Additionally, Gitari et al. investigated how the pH value affects the dissolution of elements and compounds during the leaching procedure, by adding known amounts of 2 M HNO<sub>3</sub> to adjust the pH value. Cr and Mo showed a pH dependency with a maximum at the pH of approx. 11. In contrast, above a pH value of 9, the concentrations of Fe, Mn, Ni and Cu in the leachate were very low.

[Drakonaki 1998] studied the behaviour of a fly ash from a power station burning lignite coal which contains high Ca and Mg concentrations. Studying leaching over 24 hours, at room temperature under continuous stirring and using a 1:10 (solid to liquid ratio, g/g), Drakonaki measured a pH of 12.6 in the leachate after membrane filtration with 0.45  $\mu\text{m}$  as pore diameter. The residue on the membrane filter was treated a second time and later a third time to produce a second and a third leachate. The results reveal that the sulfur compound decreased substantially, Ca concentrations slightly increased, Cr and Ni concentrations decreased, whereas the pH value remained approximatively stable.

[Ugurlu 2004] tested one ESP ash from a lignite-fired power plant at a solid to liquid ratio of 1:5 (g/g) with demineralized water for 2 hours and at temperatures of 23 °C, 40 °C and 50 °C. Only the concentrations of Na and K increased by temperature for a factor of approx. two, when 23 °C and 50 °C are considered, whereas the concentrations of Ca, Mg, sulfate and the heavy metals decreased to varying degrees.

[Yilmaz 2015] studied the leaching of ESP ashes from three lignite-fired power stations with demineralized water at a solid to liquid ratio of 1:20 (g/g), room temperature and over 18 h and analysed their residues after the leaching. For fly ashes with CaO concentrations of 12.8 % and 32.2 % ettringite (a crystalline phase of calcium alumina sulfate hydroxyl hydrate) crystallized as needles within the leachate under alkaline pH values. It could be detected by x-ray diffraction, whereas for a CaO content of 2.4 % of another lignite coal fly ash no formation took place.

## **2.2 Impact of ESP ash on the properties of MEA solutions**

ESP ashes affect the properties of MEA solutions in various ways, most importantly through the formation of degradation products dissolved in the liquid and the formation of volatile ammonia.

Chi [Chi 2000], who studied the oxidative degradation of MEA, mentioned that iron can be leached from fly ash as a possible source of ferrous iron ( $\text{Fe}^{2+}$ ), but did not publish any data.

Da Silva et al. [da Silva 2012] assessed the impact of fly ash on the formation of degradation products using ESP ash from a coal-fired power station. They applied a solid to liquid ratio of approx. 1:300 (g/g), using 5 M MEA with a loading of 0.4 mol  $\text{CO}_2$ /mol MEA and operating at

55 °C for 213 hours with sparged air. The loss of amine amounted to roughly 9 % for this time period. The authors assumed that metals from the fly ash are dissolved and catalyse degradation. The loss of amine without the dosage of fly ash under similar operating conditions was around 5 %. Injecting iron as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  to 1 mM iron increased the amine loss for the same time period to around 23 %.

[Schallert 2013] first applied the leaching standard [EN 12457-4 2003-1] and 5 M MEA solutions as liquids in order to study what can be dissolved from ESP ashes. ESP ashes were sampled from European hard coal-fired power stations, all equipped with high dust SCR and wet FGD as the last cleaning device. [Schallert 2013] analysed the compositions of the ESP ashes, while studying the leachate quality at a solid to liquid ratio of 1:10 (g/g) after 24 hours at room temperature with **1**) demineralized water (4 ESP ashes), with **2**) 5 M MEA non-loaded (3 ESP ashes) and **3**) 5 M MEA  $\text{CO}_2$  loaded were described for 4 ESP ashes. Based on lessons learned from initial leaching results, the approach was in turn adapted for each ESP ash when delivered, each time with fresh, rich loaded 5 M MEA solvent and with increasing analytical amount especially for heavy metals. For one ESP ash, Schallert examined the effects of loading, the solid to liquid ratio, the leaching time, and temperature. For another one Schallert assessed the influence of added heat stable salts (HSS) regarding the dosage of formic and oxalic acid. The results regarding the behaviour of Fe were:

- Each ESP released at 1:10 (g/g)/24 h/22 °C significantly more Fe from 5 M MEA rich loaded compared to 5 M MEA non-loaded (factor 2-4.4), compared to demineralized water to a factor of more than 900, specific for each ESP ash,
- One rich solution dissolved more than the lean one,
- most leaching occurred within 24 h, but there was still a slight increase compared to 192 h,
- the ratio of solid to liquid, changed from 1:10, 1:50 to 1:200 (g/g), decreased the Fe concentration nearly linearly,
- a temperature increase from 22 °C to 50 °C only slightly raised the concentration level of Fe,
- there seemed to be no impact of formic acid on the leachate quality at all, and
- oxalate reduced the concentration level of Fe and affected the concentration level of Ca, Mg, V and phosphate in the given ESP ash sample.

[Chandan 2014] described the results of running 4 carbon capture reactors in parallel operation. The reactors were filled with 150 ml 5 M MEA, kept stable at 80 °C, and loaded with CO<sub>2</sub> to a rich solution by sparging a mixture of air containing 15 % CO<sub>2</sub>. Chandan et al. conducted one blank test and 5 runs with added, different ESP ashes (from one lignite-fired and four hard coal-fired power plants) at a solid to liquid ratio of 1:100 (g/g) for 144 or 165 hours. They determined the concentration of some degradation products daily, but the concentration level of Fe only at the end of operation. No other heavy metal or other macroscopic, inorganic elements were analysed. When fly ash was present, then a significant enhancement of several degradation compounds occurred. The authors suspected that the leached Fe causes this enhancement. Between 4 and 10 mg Fe per kg MEA solution were measured under the leaching conditions of 1:100 (solid to liquid ratio, g/g), 80 °C and after roughly 150 hours. There is no correlation of these Fe concentrations with the respective levels of Fe in the fly ash samples.

To identify how the degraded 5 M MEA solution of CC pilot plants affects the leachability of Fe from ESP ash, [Schallert 2014] took a fly ash sample from the ESPs of 2 different hard coal-fired power stations, each equipped with a CC plant, and a sample of their lean solutions. Due to the different time of operation and the site specific parameters, the amount of inorganic and organic heat stable salts was quite different and the concentrations of Fe, Ni and Cr also differed significantly. Therefore, both 5 M lean MEA solutions were treated at laboratory scale by ion exchange using a weak acid ion exchanger (Lanxess TP 207) to remove ferrous iron (Fe<sup>2+</sup>), Ni<sup>2+</sup> as much as possible and slightly Mg<sup>2+</sup> and Ca<sup>2+</sup> from the solution. This treatment did not affect the anionic degradation products. Together with these two lean degraded, but treated 5 MEA solutions, Schallert et al. used a fresh lean 5 M MEA solution for a parallel leaching of both ESP ashes under standard conditions (1:10 (g/g), room temperature and 24 h). Compared to the fresh lean 5 M MEA solution, both degraded, treated ones released Fe less than a factor 1.5 from both ESP ashes, but the much higher degraded solution dissolved just 10 % more iron from the ESP ashes compared to lower degraded one. Thus, the increase of degradation products affects the dissolution of iron from ESP ashes, but most likely not exponentially and not linearly. Additionally, Schallert et al. conducted parallel leaching tests with both degraded, treated lean 5 M MEA solutions at 1:10 and room temperature with 24, 48 and 192 hours and secondly at room temperature and 24 h with solid to liquid ratios

(g/g) of 1:10, 1:50 and 1:200. These results are not identical to, but still confirm former investigations [Schallert 2013].

The design of the CC pilot plants differs quite a lot from each other, with respect to the equipment for the flue gas cleaning, flue gas flow, liquid inventory (abbreviated inv.) and the flue gas composition, e.g. the concentration of particulate matter. [Schallert 2016] highlighted that a solid concentration in the liquid amine solution is reached by time of operation depending on the flue gas flow, the liquid inventory and the absorbed particulate matter from the flue gas. The accumulated fly ash mass can be estimated when the concentration of particulate matter entering the absorber column and the removal efficiency are known. Assuming that 1 mg/m<sup>3</sup> particulate matter is rejected in the absorber column, then it takes roughly 6000 hours to accumulate a solid mass of 1 g/l based on a specific enrichment factor (sEF) of 0,167 m<sup>3</sup>/(l<sub>inv</sub>\*h). This factor can be calculated for EnBW's pilot plant at Heilbronn based on published data from [Rieder 2013]. To have 3.4 g ESP ash/l [da Silva 2012] or 10 g/l [Chandan 2014] accessible for leaching, it needs even more time or higher absorbed masses. In an additional study, [Schallert 2016] assessed the impact of the solid concentration on dissolved heavy metals for one ESP ash and a lean 5 M MEA solution for the ratios (solid to liquid, g/g) of 1:10, 1:50, 1:500 and 1:2000. The objective was to identify which heavy metals apart from Fe will be still detectable after 24 hours of leaching at room temperature based on a fly ash concentration of approx. 500 mg/kg. They found that the concentration of Fe was 1.1 mg/l and the concentrations of V, Cr, Mn and Cu were below 50 µg/l.

As described in the same publication, the authors conducted two additional experiments, based on solid to liquid ratios of 1:50 and room temperature, to help distinguish between "old" absorbed masses and "fresh" ones. Both experiments lasted 96 h, but while the first used the total mass of ESP ash from the beginning, the second started with a ratio of 1:200 for 24 h and increased the mass of ESP ash every 24 h, reaching the same mass as the first one by the end of the experiment. For the lower residence time of 60 hours on average the Fe concentration amounted to 19 mg/l compared to 20 mg/l for the residence time of 96 hours. This experiment was repeated with a solid to liquid ratio of 1:500 for 96 h at room temperature and 1:2000 for 24 h and three identical additions of mass every 24 h. The Fe concentrations in the leachates differed from 2.6 mg/l for 60 hours to 3 mg/l Fe for 96 hours averaged residence time. These results suggested that the accumulated mass of particulate matter mainly determines the concentration level of e.g. Fe in the leachate.

### 2.3 Fly dust properties after wet desulfurization plants

Two properties of the fly dust should be considered: the concentration of particulate matter in the emitted flue gas behind all cleaning devices and the particle size distribution (PSD) of these emitted particles. Both properties are linked to each other. Each time when the limit for the emission of particulate matter is reduced for a coal-fired power plant and a technical improvement is retrofitted to increase the particulate removal efficiency, then the PSD of the emitted particulate matter is also changed. The emitted mass of particulate matter is reduced because mainly bigger particles are captured by the improvement. Different flue gas cleaning devices behind coal-fired power stations, different dry bottom furnaces and, of course, different fly ash compositions lead to bandwidths of the emitted particulate masses and of the particle size distributions.

[Markowski 1980] at first, confirmed by [McElroy 1982] measured the PSD at the outlet of ESPs, which was the last cleaning device before stack for coal-fired power stations at that time. The PSD is bimodal with a submicron maximum around  $0.1\ \mu\text{m}$  and another one around  $3\ \mu\text{m}$  diameter. The lower diameters between  $0.05$  and  $1\ \mu\text{m}$  were continuously measured by an electrical aerosol analyser and the larger ones up to  $10\ \mu\text{m}$  with a cascade impactor. The submicron mode ranged from  $0.2$  to  $2.2\ \%$  of the total fly ash mass at the outlet of the ESP. [Linak 2002] identified three modes for the PSD behind a coal-fired power station with ESP and a wet desulfurization plant (FGD) using different detecting techniques. Fly ash particles with diameters above  $5\ \mu\text{m}$  are mainly reduced to some extent by the FGD, but the concentration of particles at lower diameters is detected at an even higher level compared to the outlet of the ESP.

The retrofit of selective catalytic reduction (SCR) plants upstream air preheater and ESP could have an impact on the emission of fine particles. At lab scale [Bao 2016] studied the fine particle concentration before and behind SCR reactor for under stoichiometric, stoichiometric and over stoichiometric dosage of ammonia regarding the  $\text{NO}_x$  concentration. Bao et al. interpreted that the increase for the fine particle concentration is due to the formation of ammonium hydrogen sulfate/ammonium sulfate as aerosols according to the operational slip of ammonia and sulfuric acid concentrations downstream the SCR plant.



At four coal-fired power stations equipped with SCR, ESP and FGD, [Li 2017] detected an increase of the PM<sub>2.5</sub> concentration when the inlet concentration (upstream FGD) was compared to the outlet concentration (downstream FGD).

The removal efficiency of those particles with low diameters, mainly below 5 µm, inside a prescrubber or a direct contact cooler upstream of the absorber column and additionally inside an absorber column for carbon capture has not been published yet.

The concentration of particulate mass, which is emitted from hard coal-fired power stations, is of special concern for the authorities, with a regulatory threshold at < 10 mg/m<sup>3</sup> particulate matter for new power stations and requirements for continuous measurements [13.BImSchV 2016]. Additionally, the concentrations of 13 elements, mainly heavy metals, are limited and regularly determined by discontinuous measurements. The element Fe is not part of these measurements.

[Meij 1994] pointed out that the particulate matter after a wet FGD plant is more than fly ash that has passed the ESP and the FGD. Instead of fly ash, Meij referred to fly dust because of droplets from the FGD that are collected together with the fly ash particles by sampling. According to [Meij 1994] approx. 40 % of the fly dust consist of fly ash, while the remaining 60 % are made up from gypsum, partly limestone, dried salts from the droplets and crystal water. Moreover, [Meij 1994] provided a classification system for all elements regarding the behaviour in the boiler and in the ducts. Class I elements do not vaporize during the combustion process, e.g. Al, Ca, Fe, K, Mg, Si, Sr and Ti. Class IIc consists of elements with a small enrichment factor of 1.3 to 2 when the concentration of fly ash is compared to the concentration in the coal ash, e.g. Cr, Mn and Na. Class IIb elements possess enrichment factors between >2 and <4, e.g. Cu, Ni, P, and V. Class IIa contains elements that are significantly enriched in ESP ash such as As, Cd, Pb, Sb, Tl and Zn, but as well Mo (with enrichment factors >4). Class III contains elements with great volatility under flue gas conditions such as Hg and Se.

This classification underlines that the composition of particulate matter should not change significantly by mass with regard to the particle size distribution for the main compounds like Fe, but will change for enriched traces like Cu, Ni and V.

Some balances for heavy metals across the wet FGD were published [Gutberlet 1984], [Meij 1994], [Fahlke 1994], and [Cordoba 2012], which contain the site specific, emitted concentrations of particulate matter during the measurement campaigns. The bandwidth

ranges from 0.05 mg/m<sup>3</sup> [Gutberlet 1984], 0.6 mg/m<sup>3</sup> [Fahlke 1994], around 1 mg/m<sup>3</sup> [Meij 1994] to around 20 mg/m<sup>3</sup> [Cordoba 2012] for the emitted concentration of particulate matter. For a Dutch dry bottom hard coal-fired power station with ESP and wet FGD [Meij 2004] determined 5 mg/m<sup>3</sup> fly dust behind FGD.

Not only the concentration of particulate matter but also the PSD is highly important when designing a commercial CC plant. There will probably be a big difference according to the concentration of fly dust and their PSD when flue gas after a new hard coal-fired power station with a completely advanced flue gas cleaning technique or after an old one with retrofitted flue gas cleaning devices is applied for carbon capture.

## **3 Materials and Methods**

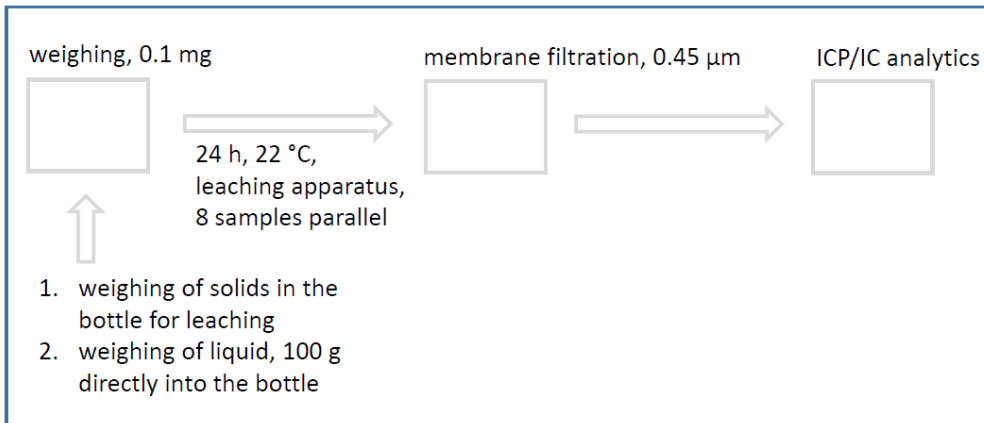
Systematic studies require the collection of sufficient material masses, yet the concentration of particulate matter behind the wet FGD is too low to reach this goal. This study uses ESP ashes as a proxy for particulate matter found after the FDG for various reasons. ESP ashes constitute several advantages. ESP ash is both readily available and easy to sample. In addition, because Fe is known as a non-volatile element [Meij 1994], there should be no big impact on the Fe concentration by the finer grain size distribution of fly ash particulate matter behind the wet FGD compared to ESP ash. The concentrations of Cr, Cu, Ni and V will be enhanced for the fly ash mass behind the wet FGD, but in principle the behaviour of these elements can be recognized, as well, when leaching will be studied with ESP ash.

### **3.1 ESP ashes**

Samples of the ESP ash are taken from the total flow of captured ESP ash to the storage silo. These are spot samples which are typical for the time of operation during sampling. The samples are kept dry in bottles of synthetic material and only opened for sampling purposes.

### **3.2 Leaching and treatment procedure**

The following standard weighing procedure is implemented to establish the necessary ratio of solid to liquid material . The fly ash mass is added into the bottle used for leaching and checked by a scientific weighing device with a read-off accuracy of 0.1 mg (Sartorius AC 211S). Then the liquid for leaching is dosed into the bottle, checked by weight. Figure 3 shows the complete treatment procedure .



**Figure 2:** Treatment procedure for the ESP ashes to be leached and analysed

The leaching takes place time dependent at room temperature using a rotary shaker from Gerhardt, type ROTOSHAKE RA 24/8 (Figure 3), following standard procedures described in [EN-12457-4]. The room temperature was not controlled, thus there might be a variation of 22 +/- 1 °C.



**Figure 3:** View into the ROTOSHAKE RA 24/8

After the foreseen time for leaching the suspensions are immediately filtered using vacuum suction technique and symmetric membranes made of cellulose nitrate with pore sizes of 0.45  $\mu\text{m}$ . The filtration technique and the membranes are delivered from Sartorius.

The clear leachates are analysed without any additional filtration by inductively coupled plasma optical emission spectroscopy (ICP-OES) technique for the element concentrations of concern following standard procedures [DIN EN ISO 11885 2009-09]. The laboratory is accredited for heavy metal analyses with this technique using an instrument of Perkin Elmer Optima 300 XL. The chloride, sulfate and carbonic acid concentrations are determined by ion chromatography (IC), using Dionex ICS 2100 with pre-column AG 15, anion column AS 15 and suppressor AERS 500 plus conductivity detector.

MEA is delivered by Merck KGaA with a purity of 99.5 %. Using demineralized water from the demin water plant of the power station, a 30 % MEA solution is set up. CO<sub>2</sub>, delivered from a gas supplier at a purity of 99.9 % (volume), is bubbled through the 30 % MEA solution in order to form a rich 5 M MEA solution, checked by acid titration.

### **3.3 Experiments**

Parallel tests are conducted using a rich loaded 5 M MEA solution for the leaching of ESP ashes from three different power plants under various conditions. In these tests, different liquids as well as different molarities of MEA solutions are compared, while also assessing the impact of three carbonic acids on the leaching of the rich loaded 5 M MEA solution. Finally, additional tests with modified solid to liquid ratios are performed. More specifically, these experiments with always the same rich loaded 5 M MEA includes the following:

- The leaching of ESP ashes in three different liquids (the rich loaded 5 M MEA, the non-loaded 5 M MEA, demineralized water) over 24 hours, at room temperature and at a solid to liquid ratio of 1:10 (g/g);
- the leaching of ESP ashes in two lower molar concentrations at a solid to liquid ratio of 1:10 (g/g);
- the leaching of ESP ashes after addition of 50 mmol/l of three carbonic acids (acetic, glycolic and oxalic acid) to three samples of the rich loaded 5 M MEA solution;
- the leaching of ESP ashes after modifications of the solid to liquid ratio, including 1:10, 1:50 to 1:200 (g/g).

The rich loaded 5 M MEA as a standard liquid for leaching is selected for two reasons: Not only does the lower pH of this solution in the absorber compared to the desorber favour the leaching of Fe [Schallert 2013] but also pilot plant inspection results [Unterberger 2013] reveals iron oxide deposits on the surfaces of packing material within the desorber.

Additional molarities of MEA solutions are examined in order to evaluate their impact on the leaching results.

Lean loaded 5 M MEA is only used for the repeatability measurements in which three solid to liquid ratios with two new ESP ashes are modified in order to assure the whole procedure of leaching and analytics.

## 4 Experimental investigations and results

This chapter presents the results of different experiments with ESP ashes from different power plants (PP). Section 4.1 deals with the composition of ESP ash samples from three PP. Section 4.2 compares the leachates of different liquids for leaching, while Section 4.3 describes the effect of MEA concentrations. Section 4.4 assesses the influence of added degradation products, followed by results of modifications of the solid to liquid ratio in Section 4.5 and the results of repeatability measurements in Section 4.6. The final section 4.7 provides a prognosis of fly ash and dissolved Fe accumulation.

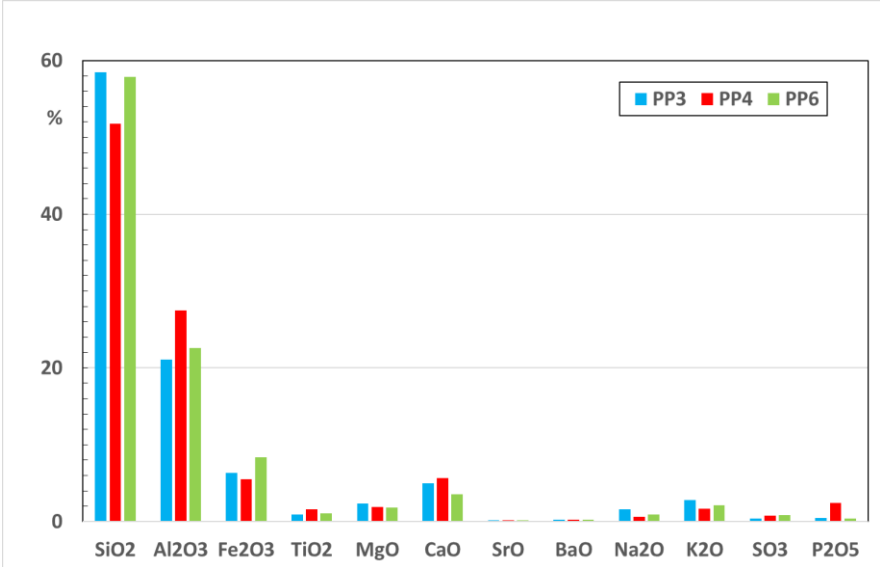
### 4.1 ESP ash composition

The three PP, from which the ESP ashes PP3, PP4 and PP6 are taken, operate hard coal-fired, dry bottom boilers and are equipped with a high dust SCR for NO<sub>x</sub> reduction, an ESP for fly ash removal and a wet FGD for the reduction of the SO<sub>2</sub> concentration. Each power plant operates a CC pilot plant after the wet FGD.

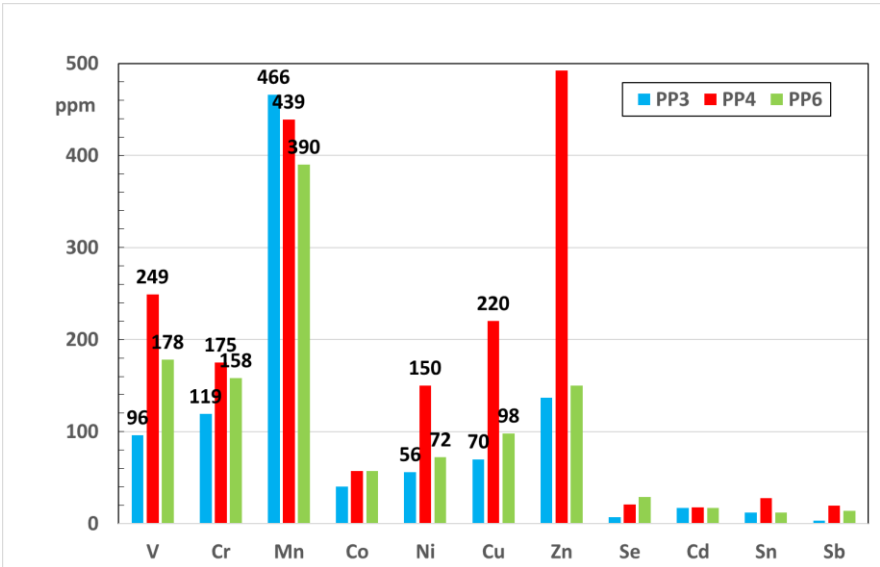
**Table 1:** Main element concentrations of ESP ashes from three different power stations, measured by x-ray fluorescence (XRF) and calculated as oxides, carbon free

		PP3	PP4	PP6	
	sampling	25.07.2012	14.02.2012	19.09.2012	
					<b>average</b>
<b>SiO<sub>2</sub></b>	%	58.5	51.8	57.9	56.1
<b>Al<sub>2</sub>O<sub>3</sub></b>	%	21.1	27.5	22.6	23.7
<b>Fe<sub>2</sub>O<sub>3</sub></b>	%	6.3	5.5	8.4	6.7
<b>TiO<sub>2</sub></b>	%	0.9	1.6	1.1	1.2
<b>MgO</b>	%	2.3	1.9	1.8	2.0
<b>CaO</b>	%	5.0	5.6	3.5	4.7
<b>SrO</b>	%	0.2	0.2	0.1	0.2
<b>BaO</b>	%	0.2	0.2	0.2	0.2
<b>Na<sub>2</sub>O</b>	%	1.6	0.7	0.9	1.1
<b>K<sub>2</sub>O</b>	%	2.8	1.7	2.2	2.2
<b>P<sub>2</sub>O<sub>5</sub></b>	%	0.5	2.4	0.4	1.1
<b>SO<sub>3</sub></b>	%	0.4	0.8	0.8	0.7

The coal is delivered from world-wide resources and burnt as coal mixtures in order to operate the boiler as efficiently as possible and to keep the power plant residues such as ESP ash below legal thresholds. The composition of the main elements for each ESP ash is listed in Table 1 and visualized as a bar chart in Figure 4. The results of the ESP ash PP4 have been previously published by [Schallert 2013], together with ESP ash samples of the power plants PP1, PP2, PP5 and a former sample of PP3. For the ESP ash PP4, no leaching data are published before.



**Figure 4:** Main element concentrations of ESP ashes from three different power stations, measured by x-ray fluorescence (XRF) and calculated as oxides, carbon free



**Figure 5:** Trace element concentrations of ESP ashes from three different power stations, measured by x-ray fluorescence



Due to the oxidative condition inside the boiler and across the complete flue gas path, nearly all solid elements (with carbon as an exception and the element concentrations < 1000 ppm) are assumed to exist predominantly as oxides. Therefore, the results are calculated as oxides. But this does not mean that free SO<sub>3</sub> or free P<sub>2</sub>O<sub>5</sub> exists inside the ESP sample. SO<sub>3</sub> is mainly connected to the oxides of the alkaline and the earth alkaline elements, which forms chemically sulfates. Similarly phosphates exist. The three ESP ashes mainly differ with regard to the concentrations of Fe<sub>2</sub>O<sub>3</sub>, CaO, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and SO<sub>3</sub>.

The variation in Fe<sub>2</sub>O<sub>3</sub> is very suitable for leaching tests. The differences in CaO will cause different free lime concentrations [Kautz 1986], which will affect the pH of the leachates with demineralized water. Sodium and sulfur as sulfate will be dissolved according to their availability at the surface of the particles. The stoichiometric ratio of SO<sub>3</sub> concentration compared to CaO concentration is probably too low to influence the pH of the leachate significantly.

The concentrations of the trace elements, including the heavy metals of concern, are shown in Figure 5. The variation of these heavy metals in the three ESP ashes, especially for V, Cu and Ni, is quite appropriate to fulfil parallel leaching experiments with different liquids and various leaching conditions (chapter 4.2 to 4.5) and then to draw conclusions from these results. The results are similar to the bandwidths of heavy metals observed in a former study of [Schallert 2013].

#### **Lessons learned from chapter 4.1**

1. The composition of each ESP ash is specific due to the composition of the coal and the impact of the furnace.
2. The variation mainly concerns iron, sodium, potassium, sulfate and phosphate in terms of main elements or compounds and vanadium, chromium, nickel and copper in terms of the other heavy metals of interest.

## **4.2 Comparison of the leachates of the different liquids for leaching**

Table 2 lists the results of the leachate composition regarding three ESP ashes and the three different liquids after parallel leaching tests. The compounds formate, which is the salt of the

formic acid HCOOH, and oxalate, which is the salt of the oxalic acid (COOH)<sub>2</sub>, are analysed to identify the concentrations caused by the 5 M MEA.

**Table 2:** Analytical results of the leachates based on demineralized water, on approx. 5 M MEA non-loaded and rich loaded MEA of three ESP ashes; **red values** are limit of detection values (LOD)

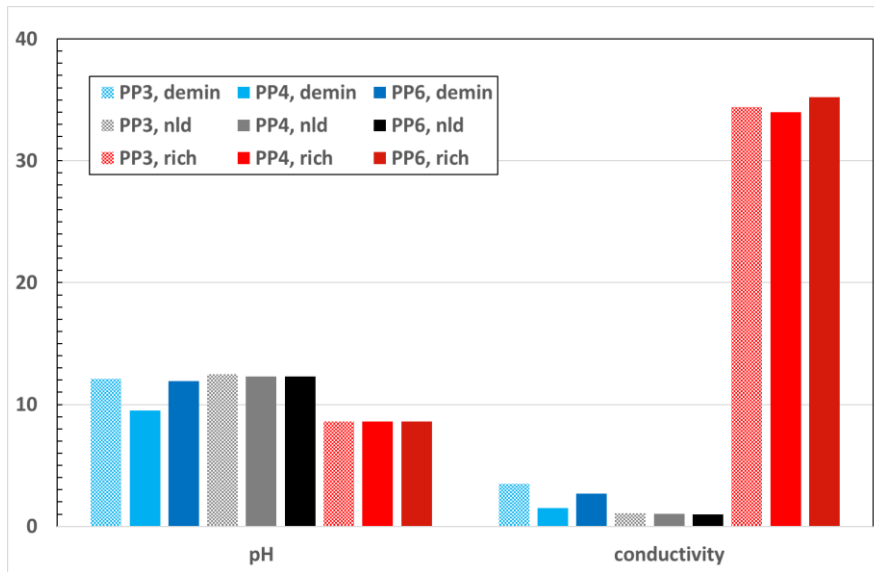
		PP3, 1:10/24 h/22 °C			PP4, 1:10/24 h/22 °C			PP6, 1:10/24 h/22 °C		
		demin	4.8 M MEA	4.4 M MEA	demin	4.7 M MEA	4.3 M MEA	demin	4.8 M MEA	4.3 M MEA
			non-loaded	rich loaded		non-loaded	rich loaded		non-loaded	rich loaded
<b>pH</b>		12.1	12.5	8.6	9.5	12.3	8.6	11.9	12.3	8.6
<b>conductivity</b>	mS/cm	3.5	1.1	34.4	1.5	1.0	34.0	2.7	1.0	35.2
<b>density</b>	g/ml	0.9942	1.0147	1.1156	0.999	1.0121	1.1152	0.9962	1.0131	1.1143
<b>alkalinity pH 7</b>	meq/kg		4757	2478		4693	2435		4748	2385
<b>alkalinity pH 4</b>	meq/kg		4814	4392		4737	4347		4805	4269
<b>loading</b>	mol/mol		0.01	0.44		0.01	0.44		0.01	0.44
<b>chloride</b>	mg/l	1	1	1	3	3	6	2	1	1
<b>phosphate</b>	mg/l	0.3	0.3	110	0.3	0.3	212	0.3	0.3	86
<b>sulfate</b>	mg/l	240	95	390	560	330	760	390	265	620
<b>formate</b>	mg/l	5	145	38	5	150	35	5	150	38
<b>oxalate</b>	mg/l	5	5	5	5	5	5	5	5	5
<b>Na</b>	mg/l	26	22	23	36	20	35	30	23	27
<b>K</b>	mg/l	6.1	4.7	6.8	10	3.9	13	15	9.7	16
<b>Mg</b>	mg/l	0.05	0.11	260	0.15	0.07	200	0.07	0.05	160
<b>Ca</b>	mg/l	380	140	37	320	68	64	350	32	63
<b>Al</b>	mg/l	0.47	0.1	0.77	13	0.2	3.6	0.36	2.1	25
<b>V</b>	mg/l	0.05	0.05	2.2	0.21	0.05	3.3	0.06	0.08	4.5
<b>Cr</b>	mg/l	0.36	0.18	1.5	0.21	0.18	1.1	0.38	0.74	2.2
<b>Mn</b>	mg/l	0.05	0.13	0.61	0.05	0.83	2.3	0.05	0.46	0.72
<b>Fe</b>	mg/l	0.08	0.73	99	0.05	8	55	0.05	22	92
<b>Ni</b>	mg/l	0.05	0.05	0.31	0.05	0.2	0.66	0.05	0.13	0.33
<b>Cu</b>	mg/l	0.05	0.49	0.43	0.05	1.5	2.7	0.05	1.1	0.83

This data set points out which elements are leached and it helps to understand why there are differences between the three different liquids with regard to the composition of the leachates. When demineralized water is used for leaching, the pH of the liquid changes over time and at the end of the leaching time the pH is characteristic for each leached ESP ash due to the different chemical composition of the ESP ashes. The non-loaded MEA solution contains about 70 % of demineralized water, but because of the high alkalinity of the approx. 5 M MEA solution the pH is high. Small amounts of leached salt, acid and/or free lime do not change this pH level significantly. The rich MEA solution absorbs fly ash particulate matter in a real CC plant during the flue gas treatment, but as a result of the CO<sub>2</sub> absorption the rich loaded MEA solution becomes intensively salty, protonated MEA molecules (HOH<sub>2</sub>C-CH<sub>2</sub>NH<sub>3</sub><sup>+</sup> or MEAH<sup>+</sup>) and negatively charged MEA carbamate molecules (HOH<sub>2</sub>C-CH<sub>2</sub>NHCO<sub>2</sub><sup>-</sup>) are formed. The alkalinity of the approx. 5 M MEA drops and the pH decreases to weak alkalinity values.

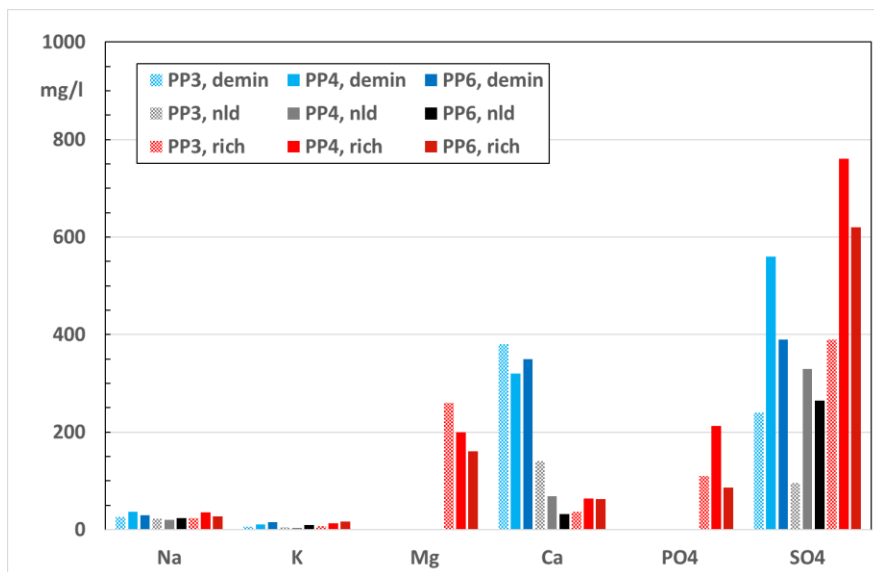
Figure 6 shows a bar chart for the pH and conductivity values of the leachates. The influence of the different ESP ash compositions causes the variation in their pH and conductivity values for the leachates of the demineralized water, whereas there is no variation for the non-loaded (nld) MEA due to the composition of the ESP ashes and only a slight impact on the conductivity values of the rich MEA solutions.

The effect of the three different liquids on pH and conductivity values is significant. Demineralized water reaches a similar pH level as the non-loaded MEA solution, but its conductivity values are higher due to the dissolved salts in the solution. The high alkalinity of the non-loaded MEA solution suppresses the dissolution of free lime. The rich MEA solution possesses high conductivity values in spite of its decreased pH level.

Figure 7 shows the concentrations of the main elements in the leachates. Calcium in the leachates varies from ESP ash to ESP ash. Nearly one order of magnitude more than the non-loaded or the rich loaded MEA solution is released by demineralized water. Magnesium is only dissolved within the rich MEA solutions, quite different for each ESP ash. When the pH will be increased again to levels above pH 10, as it will be for the lean solution, then the  $Mg^{2+}$  concentrations will drop down according to the low solubility of magnesium hydroxide  $Mg(OH)_2$ . Taking into account  $Mg^{2+}$  concentrations as detected in the leachates of the rich MEA solutions, based on 100 g ESP ash per kg rich solution, then precipitation of  $Mg(OH)_2$  will occur in the lean solution. Phosphate, which is mainly  $HPO_4^{2-}$  under these conditions [Holleman-Wiberg 1985, page 653], as well only occurs in the rich MEA solutions, varying specifically for each ESP ash. There is variation in the leachates for Na and K, but only due to their ESP ash composition. Besides Ca and sulfate no other impact can be attributed to the different liquids. The concentrations of sulfate in the leachates differ from liquid to liquid and from ESP ash to ESP ash.



**Figure 6:** pH values and conductivity results (mS/cm) in the leachates from three different liquids and three different ESP ashes

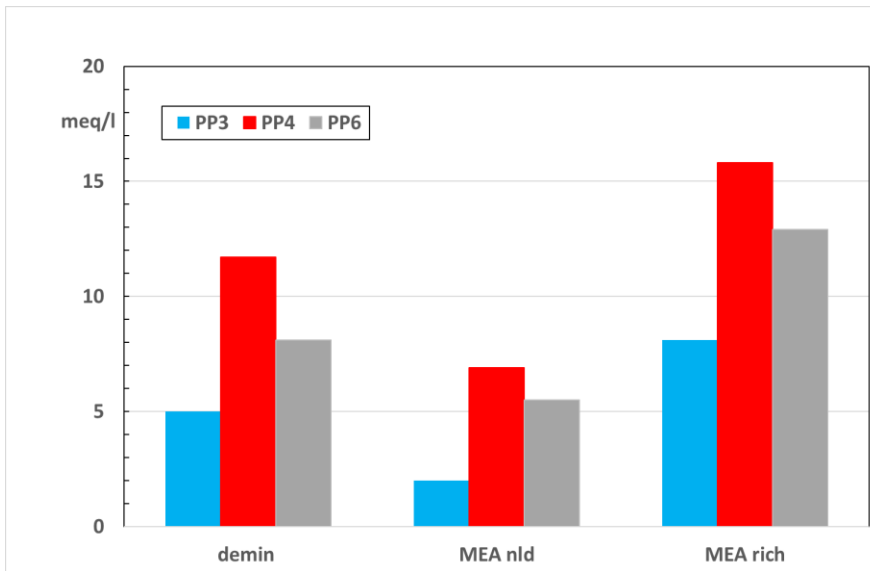


**Figure 7:** Main element concentrations in the leachates from three different liquids and three different ESP ashes

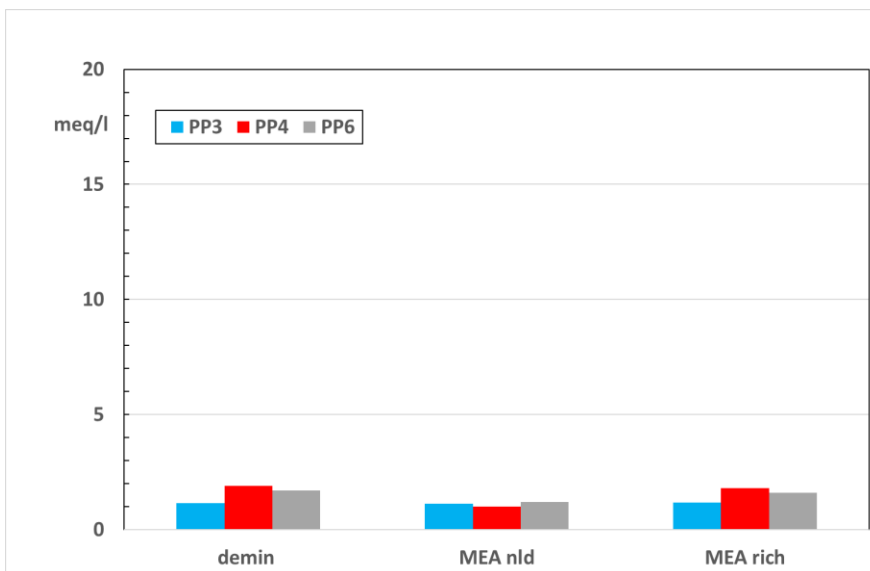
The highest concentration of sulfate is found in the ESP ash of PP4, the lowest in that of PP3. This pattern is the same for all liquids and it indicates that there are several parameters aside from temperature and pH value that influence the solubility of sulfate in the different solutions:

- The total concentration of sulfate in the ESP ash,
- the type of compound releasing sulfate to the leachate e.g.

- sodium and potassium sulfates from the surface of the particles,
- condensed sulfuric acid deposited at the surface of the particles,
- anhydrite ( $\text{CaSO}_4$  without crystal water) formed from free lime and
- formed  $\text{MgSO}_4$ , when the coal partially contains dolomite  $\text{CaMg}(\text{CO}_3)_2$  instead of limestone  $\text{CaCO}_3$ , and
- solubility effects by the law of mass action.



**Figure 8:** Milliequivalent concentrations in the leachates for sulfate from three different liquids and three different ESP ashes

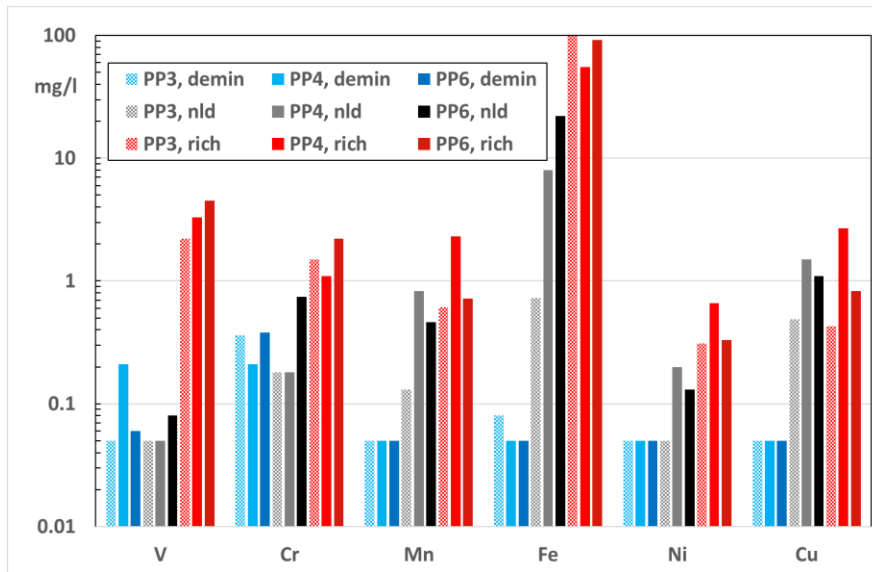


**Figure 9:** Milliequivalent concentrations in the leachates for the sum of Na and K from three different liquids and three different ESP ashes

Na- and K-sulfates are highly soluble in water and water-like solutions, whereas Ca-sulfate is only partly soluble. Considering the equivalent concentration of the different ions (Table 3) in these leachates, there is a big surplus of sulfate for PP4 and PP6 (Figure 8) when compared to the sum of Na and K (Figure 9). The sulfate concentrations in the leachates of demineralized water and non-loaded MEA are mainly related to Ca, but for the rich MEA solution Mg most likely contributes strongly. How much sulfate still derives directly from the sulfuric acid at the surface of the particles, when leaching started, cannot be estimated from the composition of the leachates. Only the time depending change of the pH to acid concentrations at the very beginning of leaching [Querol 2000] - even though it does not last very long - is a clear indicator for leached acid quantities. The dissolved alkalinity of the free lime or of the approx. 5 M MEA solutions immediately neutralizes the solution, when acid is leached.

The concentrations of Al in the leachates vary quite strongly between the three ESP ashes of all three liquids (Table 2). The number of leached ESP ashes is probably too low to recognize a systematic behaviour, but the results indicate that the glass matrix of the fly ash particulate matter also undergoes leaching.

Figure 10 shows the results of the heavy metals determined in the leachates. In terms of the results for demineralized water, only the concentrations of Cr for all 3 ESP ashes are between 0.2 and 0.4 mg/l. For Cu, Mn and Ni all values are below the LOD of 0.05 mg/l. The values for Fe are between <0.05 and 0.08 mg/l and for V between <0.05 and 0.2 mg/l. The leaching with the non-loaded MEA solution does not raise the concentration for V and Cr, but for all the other elements with varying effect regarding the different ESP ashes. Considering the average values across the results of 3 ESP ashes, there is an enhancement of approx. 0.05 to 10 mg/l for Fe, of 0.05 to 1.0 mg/l for Cu, of 0.05 to 0.5 mg/l for Mn and of 0.05 to 0.1 mg/l for Ni. Leaching is even further enhanced by the rich loaded MEA solution. Fe is enriched from 10 to 82 mg/l on average for the 3 ESP ashes, Cr from 0.4 to 1.6 mg/l, Cu from 1.0 to 1.3 mg/l, Mn from 0.5 to 1.2 mg/l, Ni from 0.1 to 0.4 mg/l, and V from 0.06 to 3.3 mg/l.



**Figure 10:** Heavy metal concentrations in the leachates from three different liquids and three different ESP ashes, the values at 0.05 mg/l (LOD value) are below LOD

By far, Fe is the heavy metal that is dissolved most intensively from ESP ashes with rich 5 M MEA solution under the leaching conditions (solid to liquid ratio of 1:10 (g/g), 24 h, 22 °C). Compared to the V concentration in the leachate, which comes second in terms of dissolution, there is still a factor of approx. 16 (mg/mg) at least.

The conversion of the concentration values (Table 3) in mg/l to milliequivalent per liter (meq/l) facilitates the recognition of a closed ion balance and potential domination by certain elements or compounds. When the meq/l cations are equal or approximately equal to the meq/l anions, then the ion balance is called closed. The hydroxide concentration is not determined, but calculated from the pH value of the leachate. The ion balance of the species in the leachates is significantly different for the three liquids, but similar for the three ESP ashes concerned to demineralized water or non-loaded MEA solution. For demineralized water there is a gap of 2.7-7.5 meq/l which is certainly related to the carbonate and hydrogencarbonate concentrations in the leachate. The non-loaded MEA points out a gap on the cation side which derives from the reaction of the base (mono ethanolamine) with water which forms MEAH<sup>+</sup> (protonated MEA molecule in water by hydrolysis) and OH<sup>-</sup> to a low extent. The variation of MEAH<sup>+</sup> in the leachates of the three ESP ashes is small. The gap of ion balance for the rich loaded MEA solution is significant and varies between 17 and 63 % of the sum of anions or as alkalinity between 4.0 meq/l (PP4) and 17.9 meq/l (PP3). The carbamate (HOH<sub>2</sub>C-CH<sub>2</sub>NHCOO<sup>-</sup>) molecule formed by the reaction of MEA with absorbed CO<sub>2</sub> in the

solution is not included into the balance, because of the high surplus, but will be considered in the discussion of the results.

**Table 3:** Analytical results of the leachates based on demineralized water, approx. 5 M MEA non-loaded and rich loaded MEA for three ESP ashes calculated to meq/l; red values are LOD values; \*values of carbonate and hydrogencarbonate added to close the ion balance

		PP3, 1:10/24 h/22 °C			PP4, 1:10/24 h/22 °C			PP6, 1:10/24 h/22 °C		
		demin	4.8 M MEA	4.4 M MEA	demin	4.7 M MEA	4.3 M MEA	demin	4.8 M MEA	4.3 M MEA
			non-loaded	rich loaded		non-loaded	rich loaded		non-loaded	rich loaded
hydroxide	meq/l	12.6	31.6	0.004	0.032	20.0	0.004	7.9	20.0	0.004
chloride	meq/l	0.03	0.03	0.03	0.08	0.08	0.17	0.06	0.03	0.03
phosphate	meq/l	0.006	0.006	2.3	0.006	0.006	4.5	0.006	0.006	1.8
sulfate	meq/l	5.0	2.0	8.1	11.7	6.9	15.8	8.13	5.52	12.9
carb. + hydrogencarb. *	meq/l	2.7		17.9	7.5		4.0	3.1		9.8
sum anions	meq/l	20.3	33.6	28.4	19.3	26.9	24.5	19.2	25.5	24.5
sodium	meq/l	1.1	1.0	1.0	1.6	0.9	1.5	1.3	1.0	1.2
potassium	meq/l	0.16	0.12	0.17	0.26	0.10	0.33	0.38	0.25	0.41
magnesium	meq/l	0.004	0.01	21.4	0.01	0.006	16.5	0.006	0.004	13.2
calcium	meq/l	19.0	7.0	1.8	16.0	3.4	3.2	17.5	1.6	3.1
aluminium	meq/l	0.05	0.01	0.09	1.45	0.02	0.40	0.04	0.23	2.78
vanadium	meq/l	0.004	0.004	0.17	0.02	0.004	0.26	0.005	0.006	0.35
chromium	meq/l	0.02	0.01	0.09	0.01	0.01	0.06	0.02	0.04	0.13
manganese	meq/l	0.004	0.01	0.04	0.004	0.06	0.17	0.004	0.03	0.05
iron	meq/l	0.003	0.03	3.5	0.003	0.43	2.0	0.003	1.18	3.3
nickel	meq/l	0.002	0.002	0.01	0.002	0.007	0.022	0.002	0.004	0.011
copper	meq/l	0.002	0.02	0.01	0.002	0.05	0.08	0.002	0.03	0.03
MEAH+ *	meq/l		25.4			22.0			21.1	
sum cations	meq/l	20.3	33.6	28.4	19.3	26.9	24.5	19.2	25.5	24.5

### Lessons learned from chapter 4.2

1. The conditions in a CC plant, which operates a 5 M MEA solution, tend to leach especially Fe from absorbed fly ash particles when the MEA is intensively loaded with CO<sub>2</sub>.
2. The other 5 studied heavy metals (V, Cr, Mn, Ni and Cu) are mobilized in the rich loaded 5 M MEA as well, but to a much lower extent. The mass concentration of V is at least a factor of 16 lower than the Fe mass concentration in the leachate depending on the ESP ash quality.
3. Besides salts like Na- and K-sulfate or anhydrite (CaSO<sub>4</sub>) the rich MEA solution dissolves Mg-sulfate and -phosphate.
4. The Al concentrations in the leachates indicate that leaching of glass occurs.
5. The gaps in the ion balances will be discussed in chapter 5



### 4.3 Effect of the MEA concentration

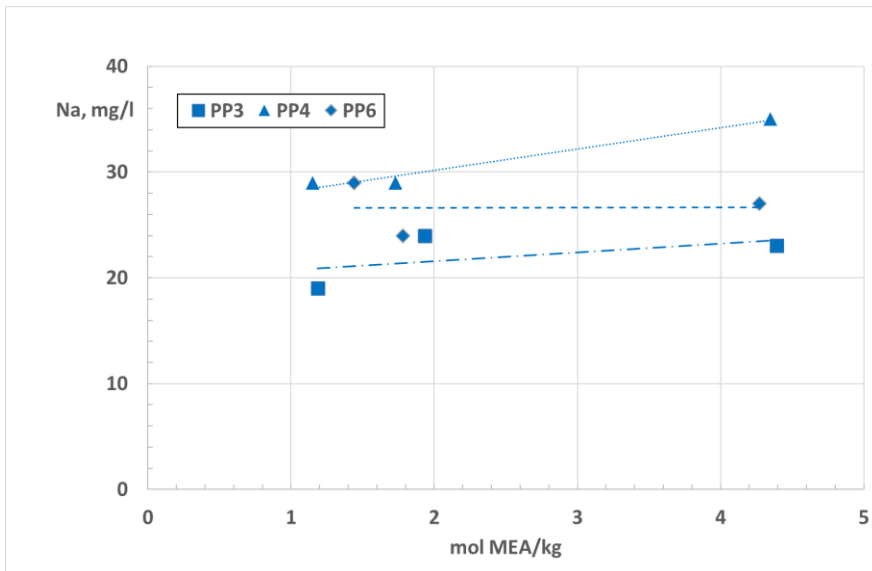
The next step is to identify which parameters influence the concentration of the heavy metals of concern, and to which extent. One parameter of interest is the MEA concentration itself. In the past, CC plants with MEA were operated at a concentration of 2-3 M [Arnold 1982] in order to match the material concept and to keep corrosion at an acceptable level. Nowadays 5 M MEA is the standard absorbing liquid and a further increase in molarity may help to reduce construction and operational costs.

**Table 4:** Analytical results of the leachates based on rich loaded MEA solutions for three ESP ashes; **red values** are LOD values

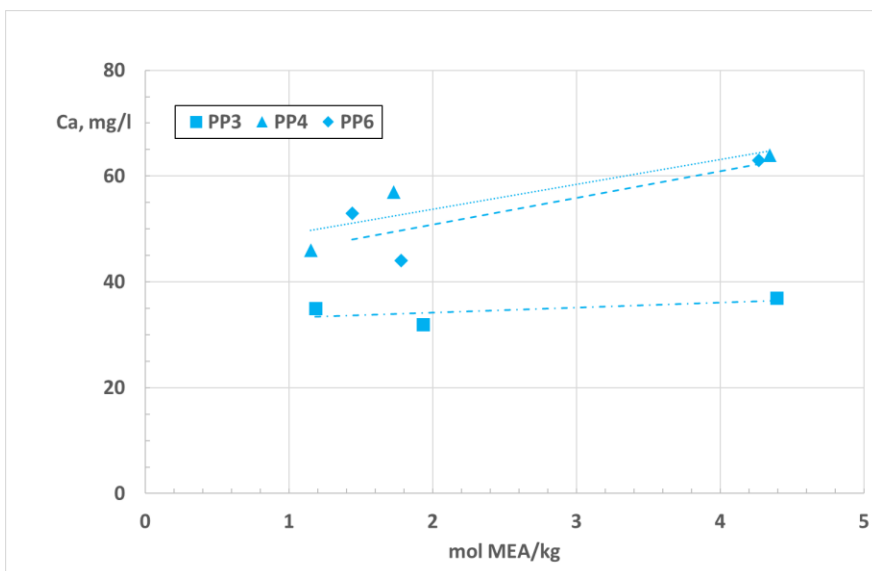
		PP3, 1:10/24 h/22 °C			PP4, 1:10/24 h/22 °C			PP6, 1:10/24 h/22 °C		
		rich MEA			rich MEA			rich MEA		
	mol/kg	1.2	1.9	4.4	1.2	1.7	4.3	1.4	1.8	4.3
<b>pH</b>		8.9	8.8	8.6	8.9	8.8	8.6	8.8	8.8	8.6
<b>conductivity</b>	mS/cm	25.8	34.2	34.4	26.0	32.6	34.0	30.1	33	35.2
<b>density</b>	g/ml	1.0313	1.0515	1.1156	1.0332	1.0466	1.1152	1.0383	1.0471	1.1143
<b>alkalinity pH 7</b>	meq/kg	711	1117	2478	668	980	2435	824	1005	2385
<b>alkalinity pH 4</b>	meq/kg	1185	1935	4392	1152	1730	4347	1440	1780	4269
<b>loading</b>	mol/mol	0.40	0.42	0.44	0.42	0.43	0.44	0.43	0.44	0.44
<b>chloride</b>	mg/l	4	17	1	6	4	6	2	9	1
<b>phosphate</b>	mg/l	67	86	110	95	129	212	31	49	86
<b>sulfate</b>	mg/l	290	440	390	490	645	760	750	530	620
<b>formate</b>	mg/l	12	17	38	10	15	35	15	18	38
<b>oxalate</b>	mg/l	5	5	5	5	5	5	5	5	5
<b>Na</b>	mg/l	19	24	23	29	29	35	29	24	27
<b>K</b>	mg/l	5.6	7.3	6.8	10	11	13	17	14	16
<b>Mg</b>	mg/l	130	180	260	130	140	200	110	100	160
<b>Ca</b>	mg/l	35	32	37	46	57	64	53	44	63
<b>Al</b>	mg/l	0.19	0.62	0.77	0.66	1.6	3.6	9.3	18	25
<b>V</b>	mg/l	1.5	1.9	2.2	2	2.4	3.3	2.9	3	4.5
<b>Cr</b>	mg/l	0.87	1.1	1.5	0.5	0.58	1.1	0.87	1.3	2.2
<b>Mn</b>	mg/l	0.12	0.24	0.61	0.36	0.69	2.3	0.05	0.32	0.72
<b>Fe</b>	mg/l	8.1	25	99	5.2	16	55	11	37	92
<b>Ni</b>	mg/l	0.16	0.23	0.31	0.39	0.47	0.66	0.23	0.2	0.33
<b>Cu</b>	mg/l	0.32	0.43	0.43	1.7	1.9	2.7	0.73	0.69	0.83

Table 4 lists the results of the leachates that are produced with different rich MEA concentrations for three different ESP ashes. These different MEA concentrations are produced from the rich loaded 5 M MEA solution by defined mixing with demineralized water, which also leads to slightly lower loading values. Those elements or compounds that are dissolved independently of three different liquids (chap. 4.2) are expected to have no relationship with the molar concentration of MEA because of the same mass to be leached.

For Na (Figure 11) and Ca (Figure 12) and also for K (Figure 13) and sulfate (Figure 14) there are different concentration levels due to the leached ESP ash and only a small or likely no dependency on the molar concentration of MEA. The straight lines are regression lines (Fig. 11-14), but their slopes are much smaller than the increase of the MEA molarity. If the rich loaded, molar MEA concentration were zero, then the concentration level of these elements or compounds would be expected to be the same as in demineralized water.

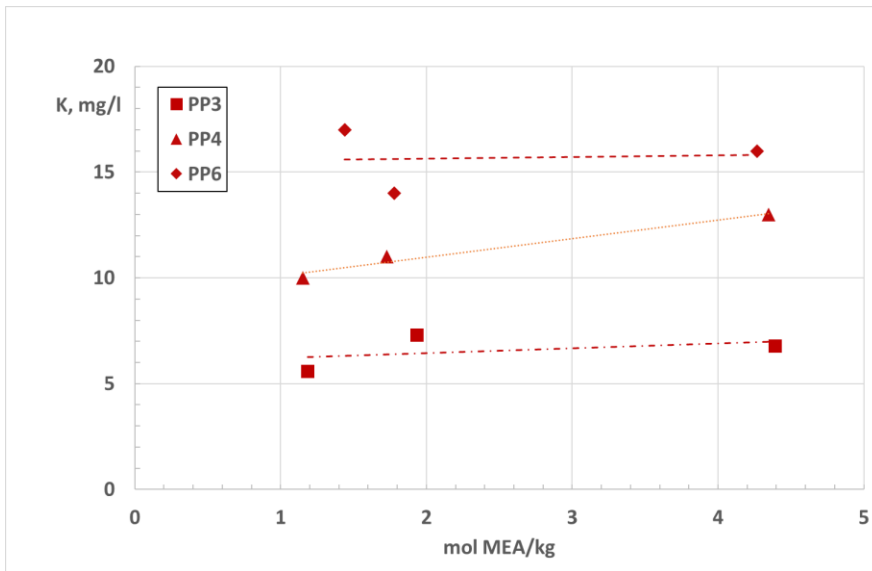


**Figure 11:** Na concentrations in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the rich loaded, molar MEA concentration

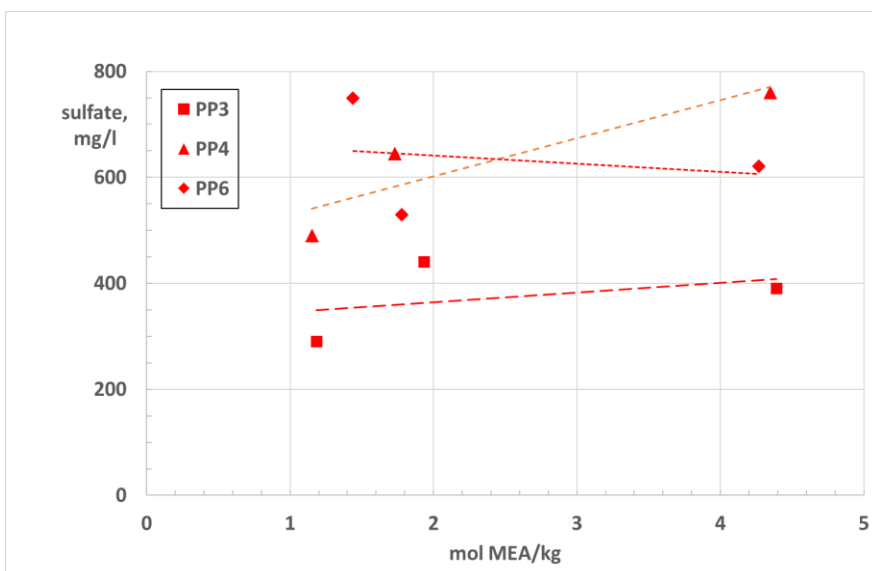


**Figure 12:** Ca concentrations in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the rich loaded, molar MEA concentration

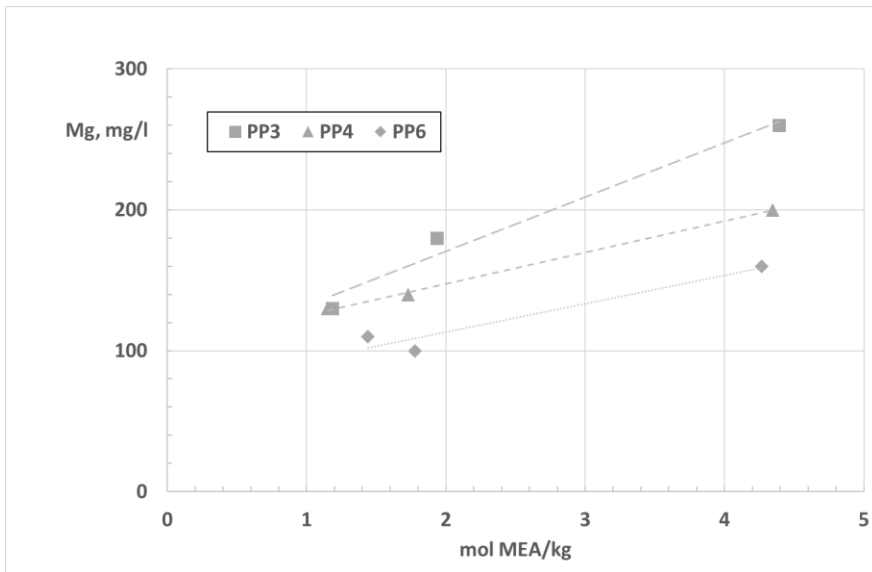
In contrast to the behaviour of Na, K, Ca and sulfate, Mg (Figure 15) and phosphate (Figure 16) are intensively dissolved depending on the molar concentration of MEA. For a lower molar, rich MEA concentration near to zero M MEA/kg, the concentrations of Mg and phosphate must drop down towards zero mg/l.



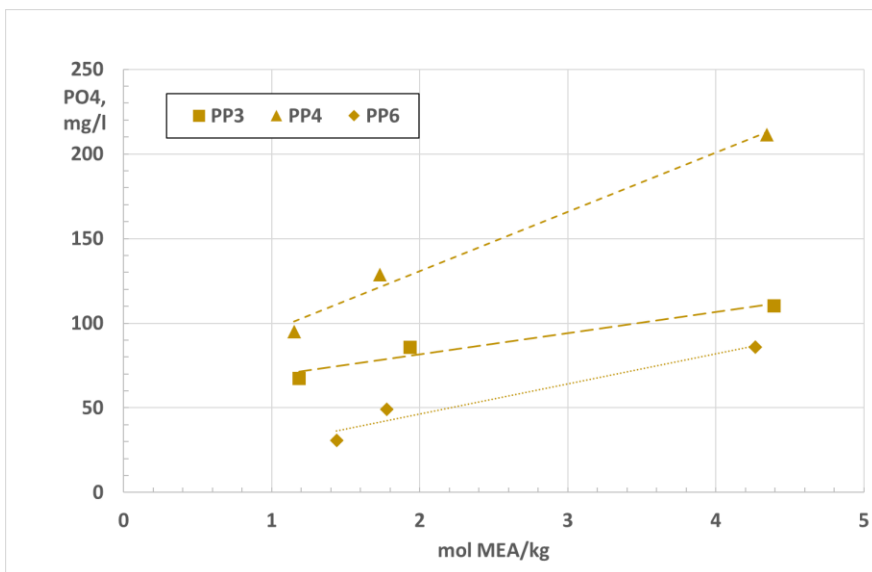
**Figure 13:** K concentrations in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the rich loaded, molar MEA concentration



**Figure 14:** Sulfate concentrations in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the rich loaded, molar MEA concentration

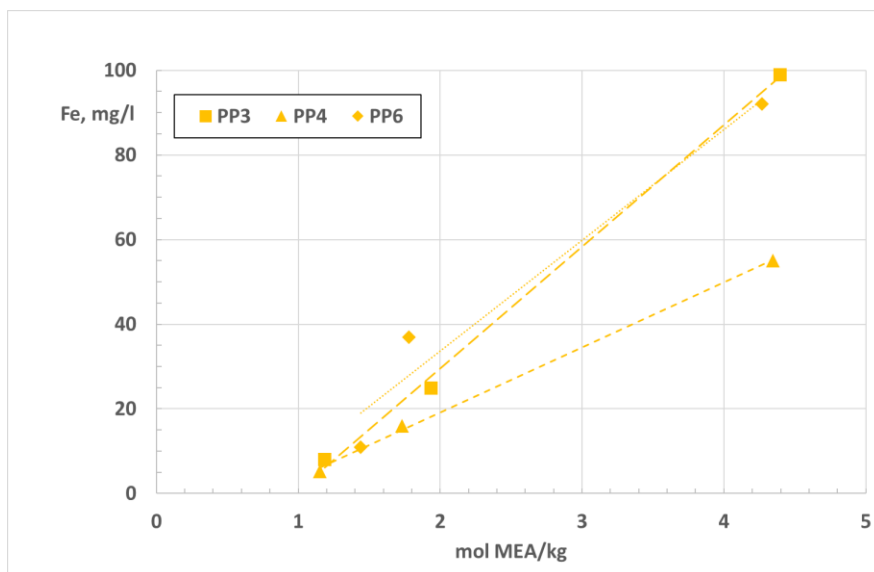


**Figure 15:** Mg concentrations in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the rich loaded, molar MEA concentration



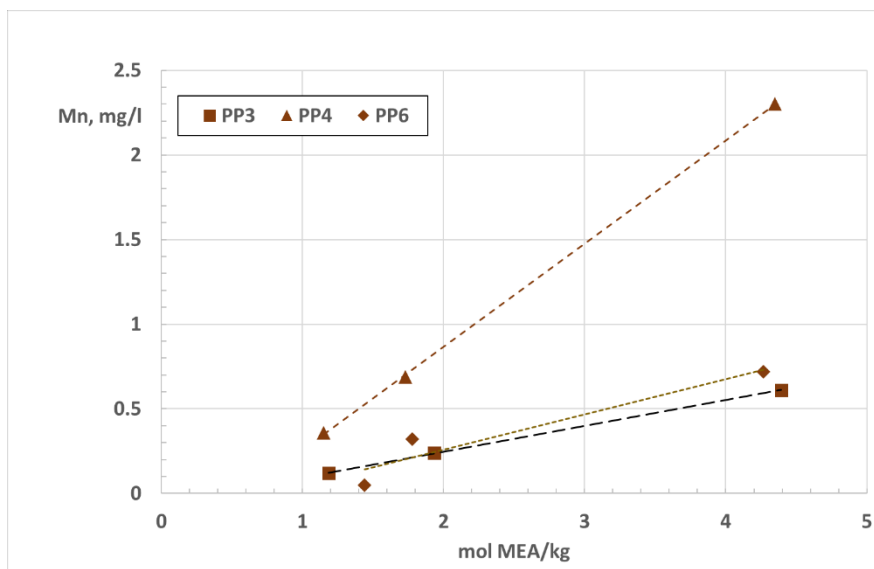
**Figure 16:** Phosphate concentrations in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the rich loaded, molar MEA concentration

The behaviour of Fe (Figure 17) looks quite similar to Mg and phosphate. The leachates of all ESP ashes possess a strong linear dependency of Fe to the molar concentration of MEA. The straight lines for Fe start from a quite small concentration, therefore only a slight increase of the Fe concentration can be expected when the rich loaded, molar MEA concentration is changed from zero to 1 mol MEA/kg. At higher molar, rich loaded MEA concentrations than experienced it can be assumed that even more Fe can be dissolved from the same mass of the ESP ash.

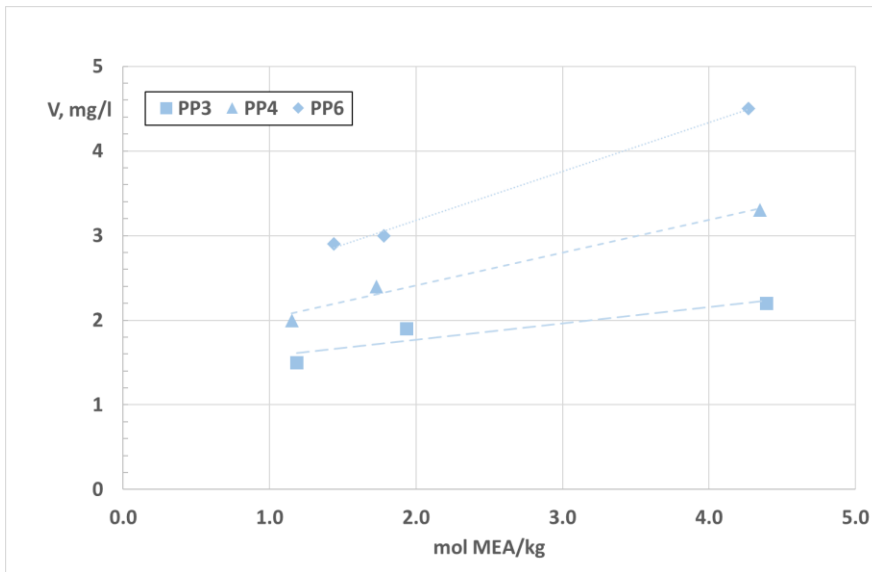


**Figure 17:** Fe concentrations in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the rich loaded, molar MEA concentration

In principle the behaviour of Mn (Figure 18) is comparable to Fe, but with much lower concentrations in the leachates and also lower slopes of the linear regression lines. The behaviour of the other heavy metals like V (Figure 19) are similar to the behaviour of Mg, but at much lower concentration levels.

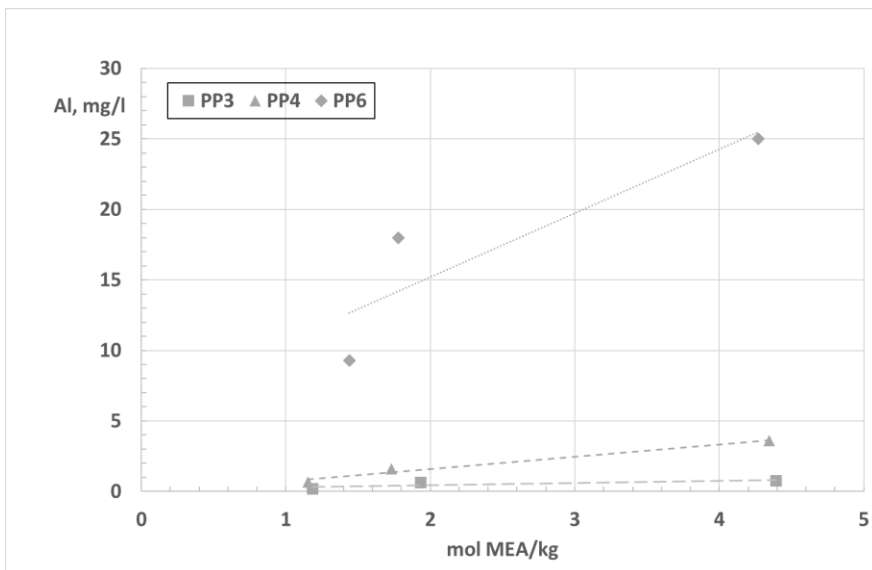


**Figure 18:** Mn concentrations in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the rich loaded, molar MEA concentration



**Figure 19:** V concentrations in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the rich loaded, molar MEA concentration

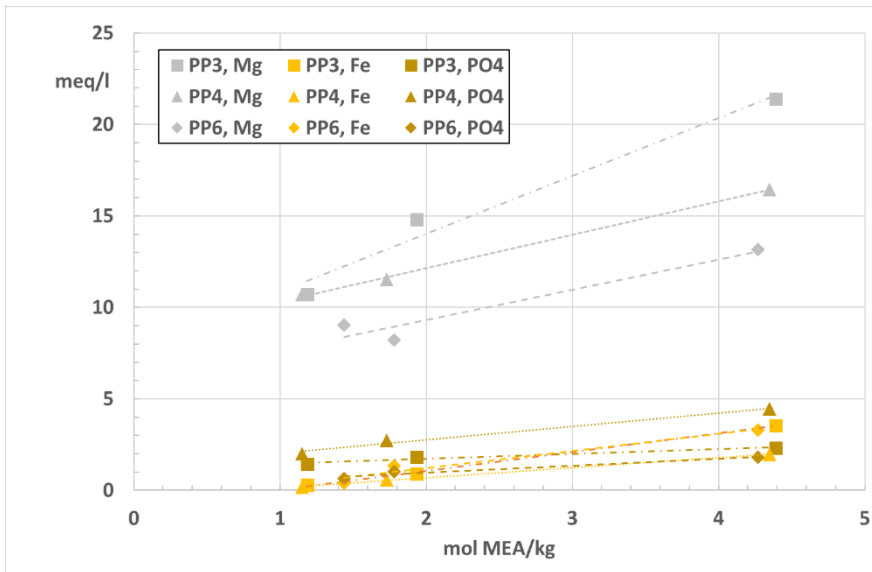
The concentration of Al clearly increases with the molar, rich loaded MEA concentration (Figure 20), but differ significantly from ESP ash to ESP ash. Leaching with even higher molar, rich loaded MEA concentration will probably attack the glass matrix more intensively.



**Figure 20:** Al concentrations in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the rich loaded, molar MEA concentration

For comparison the equivalent concentrations of  $Mg^{2+}$ ,  $Fe^{2+}$  and  $HPO_4^{2-}$  are set in relation to the rich loaded, molar MEA concentration (Table 5, Figure 21). The Mg milliequivalent concentration predominates, maybe, partially related to phosphate. The slope of the

regression lines differs for each ESP ash and for each element or compound. The Mg milliequivalent concentration shows the highest slopes of the regression lines, followed by Fe and phosphate.



**Figure 21:** Milliequivalent concentrations of  $Mg^{2+}$ ,  $Fe^{2+}$  and  $HPO_4^{2-}$  in the leachates of ESP ashes from different power plants (PP3, PP4, PP6) as a function of the molar, rich loaded MEA concentration

Based on all data no correlation seems to exist between Fe and phosphate. Possibly, the number of samples with different molar, rich loaded MEA concentration is too low to observe such a correlation; alternatively, the variation due to the compositions of the ESP ashes may be, too large.

The ion balance is not closed for all leachates (Table 5). The difference of approx. 7.5 % for cations of the sample 1.4 M MEA (PP6) is the only acceptable one because there is a small surplus of  $MEA^+$ . The alkalinity concerned to carbonate and hydrogencarbonate, which is missing in the balance of the anions, rises with the increasing molarity of the rich MEA solution. Each ESP ash has its own specific pattern.

**Table 5:** Analytical results of the leachates based on rich loaded MEA with different molarities for three ESP ashes calculated to meq/l; red values are LOD values; \*values of carbonate and hydrogencarbonate or MEAH<sup>+</sup> added to close the ion balance

		PP3, 1:10/24 h/22 °C			PP4, 1:10/24 h/22 °C			PP6, 1:10/24 h/22 °C		
		rich MEA			rich MEA			rich MEA		
	mol/kg	1.2	1.9	4.4	1.2	1.7	4.3	1.4	1.8	4.3
hydroxide	meq/l	0.008	0.006	0.004	0.008	0.006	0.004	0.006	0.006	0.004
chloride	meq/l	0.1	0.5	0.0	0.17	0.11	0.17	0.06	0.25	0.03
phosphate	meq/l	1.4	1.8	2.3	2.0	2.7	4.4	0.6	1.0	1.8
sulfate	meq/l	6.0	9.2	8.1	10.2	13.4	15.8	15.6	11.0	12.9
carb. + hydrogencarb. *	meq/l	6.2	7.2	17.8	2.6	0.8	4.1		3.2	9.8
sum anions	meq/l	13.9	18.8	28.4	15.0	17.0	24.5	16.3	15.5	24.5
sodium	meq/l	0.8	1.0	1.0	1.3	1.3	1.5	1.3	1.0	1.2
potassium	meq/l	0.14	0.19	0.17	0.26	0.28	0.33	0.43	0.36	0.41
magnesium	meq/l	10.7	14.8	21.4	10.7	11.5	16.5	9.0	8.2	13.2
calcium	meq/l	1.7	1.6	1.8	2.3	2.8	3.2	2.6	2.2	3.1
aluminium	meq/l	0.02	0.07	0.09	0.07	0.18	0.40	1.0	2.0	2.8
vanadium	meq/l	0.12	0.15	0.17	0.16	0.19	0.26	0.23	0.24	0.35
chromium	meq/l	0.05	0.06	0.09	0.03	0.03	0.06	0.05	0.08	0.13
manganese	meq/l	0.01	0.02	0.04	0.03	0.05	0.17	0.00	0.02	0.05
iron	meq/l	0.3	0.9	3.5	0.2	0.6	2.0	0.4	1.3	3.3
nickel	meq/l	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01
copper	meq/l	0.01	0.01	0.01	0.05	0.06	0.08	0.02	0.02	0.03
MEAH+ *	meq/l							1.2		
sum cations	meq/l	13.9	18.8	28.4	15.0	17.0	24.5	16.3	15.5	24.5

### Lessons learned from chapter 4.3

1. The Fe concentration in the leachate depends linearly on the molar, rich loaded MEA concentration. It is probable that at 7 M MEA an even stronger leaching of Fe will occur.
2. The rich loaded MEA solution with increasing molar concentrations fosters the dissolution of Mg from ESP ashes, similar to Fe or phosphate.
3. The concentrations of V, Cr and Mn depend on the molar, rich loaded MEA concentration.
4. Ca and sulfate are partly soluble according to the solubility of CaSO<sub>4</sub> under these conditions.
5. Na and K are dissolved to nearly the same extent independent of the molar, rich loaded MEA concentration.
6. Glass leaching increases with increasing molar, rich loaded MEA concentration.



#### 4.4 Influence of added degradation products

The following section deals with the influence of degradation products during operation, when the MEA concentration has already been selected and fixed.

Four different liquids are used for the leaching of each ESP ash: as a standard the rich loaded MEA without any dosage, secondly added with 50 mmol/l acetic acid, thirdly with 50 mmol/l glycolic acid and fourthly with 50 mmol/l oxalic acid. These three dotted liquids simulate separately the effect of accumulated degradation products on the dissolution of heavy metals and on macro elements from three ESP ashes under the standard leaching conditions of 1:10 (solid to liquid ratio, g/g), 24 hours and room temperature. The analytical results of the leachates are listed in Table 6.

There is no impact of these dosages on the pH of the leachate and on the loading of the liquid. Added acid is immediately neutralized by the alkalinity of the rich loaded MEA solution. Organic heat stable salts (HSS) are formed. When oxidative degradation of the MEA during CC operation occurs, the carbonic acids are immediately neutralized by MEA molecules. These MEA molecules are no longer available for regeneration. According to an increased amount of dissociated salts, the values for conductivity are slightly higher than those of the liquid without any dosage of acid. Additionally, the analytical parameter alkalinity at pH 4, which is the total alkalinity in the solution by acid titration to pH 4, slightly decreases due to the dosed amounts of acid. That indicates a small loss of the MEA concentration due to the formation of heat stable salts. The concentration of oxalate is significantly reduced compared to the dosed concentration. The concentration levels mainly differ from ESP ash to ESP ash and from each added acid when compared to no dosage of acid. Only for Na, K, Cu and Ni no significant changes are noticeable. All other elements or compounds show an enhancement or a reduction compared to the concentration level in the leachate of the rich loaded MEA without any dosage. Oxalic acid changes the concentrations of phosphate, Mg and Ca significantly. Phosphate is slightly increased by acetic and glycolic acid, but intensively raised by oxalic acid.

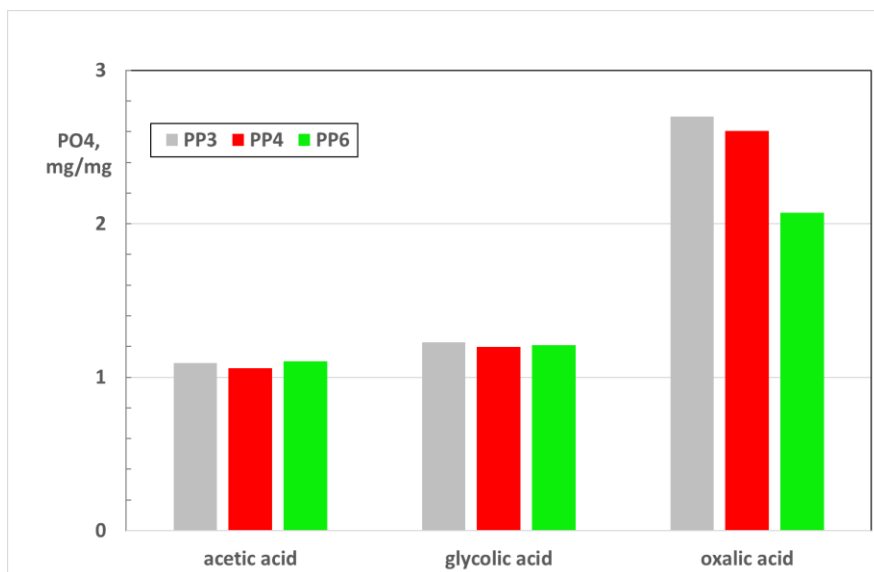
**Table 6:** Analytical results of the leachates based on rich loaded MEA solutions added with three different acids and applied for leaching of three ESP ashes; **red values** are LOD values

50 mmol/l acid added		PP3, 1:10/ 24 h/ 22 °C rich 4.4 M MEA				PP4, 1:10/ 24 h/ 22 °C rich 4.3 M MEA				PP6, 1:10/ 24 h/ 22 °C rich 4.3 M MEA			
		0	acetic acid	glycolic acid	oxalic acid	0	acetic acid	glycolic acid	oxalic acid	0	acetic acid	glycolic acid	oxalic acid
		pH		8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6
conductivity	mS/cm	34.4	34.7	35.0	35.3	34.0	35.0	34.8	35.2	35.2	35.1	35.1	36
density	g/ml	1.1156	1.1138	1.1179	1.1138	1.1152	1.1158	1.1179	1.1153	1.1143	1.1136	1.119	1.1169
alkalinity pH 7	meq/kg	2478	2412	2410	2345	2435	2340	2374	2351	2385	2360	2355	2333
alkalinity pH 4	meq/kg	4392	4334	4277	4210	4347	4269	4260	4190	4269	4265	4215	4170
loading	mol/mol	0.44	0.44	0.44	0.44	0.44	0.45	0.44	0.44	0.44	0.45	0.44	0.44
chloride	mg/l	1	3	2	1	6	3	7	5	1	2	2	1
phosphate	mg/l	110	120	135	297	212	224	254	552	86	95	104	178
sulfate	mg/l	390	495	445	345	760	815	1050	750	620	710	855	620
formate	mg/l	38	28	31	25	35	30	32	40	38	27	30	25
oxalate	mg/l	5	5	5	3070	5	5	5	2460	5	5	5	3820
Na	mg/l	23	22	22	24	35	35	36	36	27	27	28	30
K	mg/l	6.8	6.8	6.8	6.8	13	13	14	15	16	17	17	17
Mg	mg/l	260	270	260	190	200	200	210	190	160	160	170	120
Ca	mg/l	37	41	40	9.5	64	85	130	10	63	68	56	8.4
Al	mg/l	0.77	0.8	2.6	1.4	3.6	6.1	18	31	25	28	32	35
V	mg/l	2.2	2.4	2.5	3.5	3.3	3.3	3.5	5.4	4.5	4.7	4.7	5.3
Cr	mg/l	1.5	1.5	1.7	1.6	1.1	1.1	1.4	2	2.2	2.2	2.4	2.3
Mn	mg/l	0.61	0.76	0.67	0.66	2.3	2.6	2.7	3.6	0.72	0.79	0.7	1
Fe	mg/l	99	110	140	61	55	63	83	80	92	100	120	85
Ni	mg/l	0.31	0.33	0.35	0.32	0.66	0.69	0.71	0.78	0.33	0.34	0.34	0.32
Cu	mg/l	0.43	0.45	0.46	0.45	2.7	2.7	2.9	3.5	0.83	0.92	0.94	0.92

**Table 7:** Normalized analytical results of the leachates based on rich loaded MEA solution results without any addition of acid and applied for the leaching of three ESP ashes with the three carbonic acids; **red values** indicate a decrease of the concentration

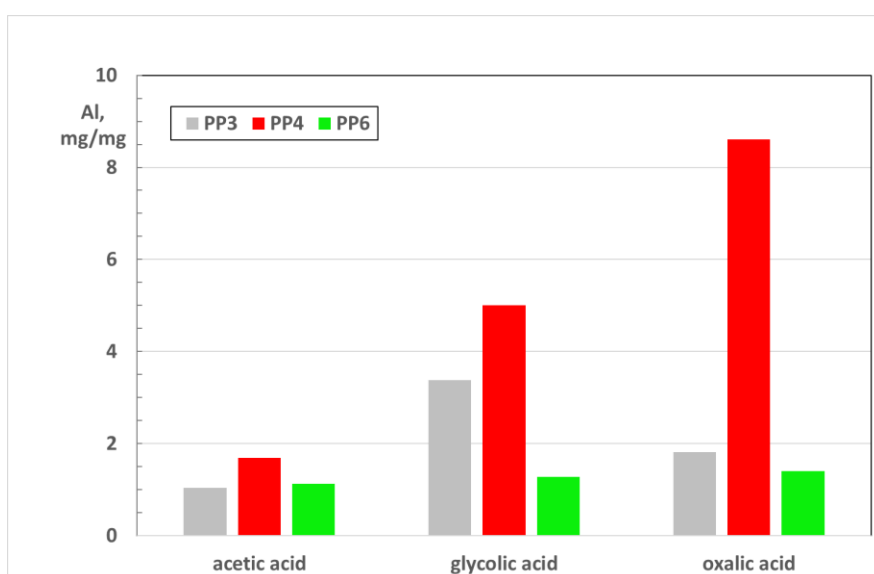
		PP3				PP4				PP6			
		50 mmol/l acetic acid				50 mmol/l glycolic acid				50 mmol/l oxalic acid			
		average				average				average			
Na	mg/mg	0.99	0.96	1.00	1.00	1.01	0.96	1.03	1.04	1.06	1.04	1.03	1.11
K	mg/mg	1.02	1.00	1.00	1.06	1.05	1.00	1.08	1.06	1.07	1.00	1.15	1.06
Mg	mg/mg	1.01	1.04	1.00	1.00	1.04	1.00	1.05	1.06	0.81	0.73	0.95	0.75
Ca	mg/mg	1.17	1.11	1.33	1.08	1.33	1.08	2.03	0.89	0.18	0.26	0.16	0.13
Al	mg/mg	1.28	1.04	1.69	1.12	3.22	3.38	5.00	1.28	3.94	1.82	8.61	1.40
V	mg/mg	1.05	1.09	1.00	1.04	1.08	1.14	1.06	1.04	1.47	1.59	1.64	1.18
Cr	mg/mg	1.00	1.00	1.00	1.00	1.17	1.13	1.27	1.09	1.31	1.07	1.82	1.05
Mn	mg/mg	1.16	1.25	1.13	1.10	1.08	1.10	1.17	0.97	1.35	1.08	1.57	1.39
Fe	mg/mg	1.11	1.11	1.15	1.09	1.41	1.41	1.51	1.30	1.00	0.62	1.45	0.92
Ni	mg/mg	1.05	1.06	1.05	1.03	1.08	1.13	1.08	1.03	1.06	1.03	1.18	0.97
Cu	mg/mg	1.05	1.05	1.00	1.11	1.09	1.07	1.07	1.13	1.15	1.05	1.30	1.11
sulfate	mg/mg	1.16	1.27	1.07	1.15	1.30	1.14	1.38	1.38	0.96	0.88	0.99	1.00
phosphate	mg/mg	1.08	1.09	1.06	1.10	1.21	1.23	1.20	1.21	2.46	2.70	2.60	2.07

In order to compare these increases in leachates of each ESP ash by the different added acids, the concentrations are normalized by the value in the leachate without any dosage (Table 7).



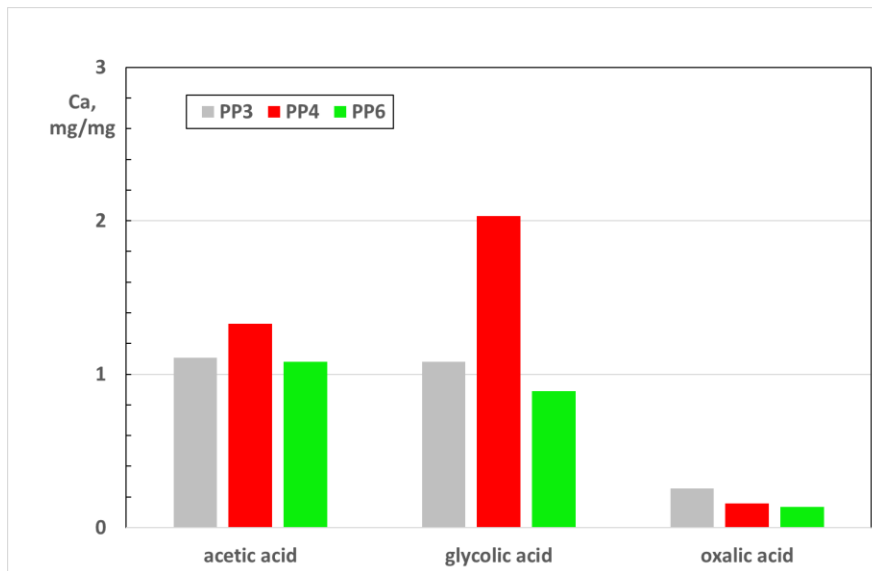
**Figure 22:** Normalized changes for phosphate in the leachates of ESP ashes from different power plants caused by the addition of different acids to the liquid before leaching

Figure 22 shows these results for phosphate. All added acids raise the concentration of phosphate in the leachate, independent of the ESP ash. Acetic acid causes a minor increase of phosphate, while the increase due to glycolic acid is slightly higher and the increase due to oxalic acid is about twice as much. The oxalic acid concentration in the leaching solution dissolves phosphate from the ESP ash particles, which confirms former results of [Schallert 2013].



**Figure 23:** Normalized changes for Al in the leachates of ESP ashes from different power plants caused by the addition of different acids to the liquid before leaching

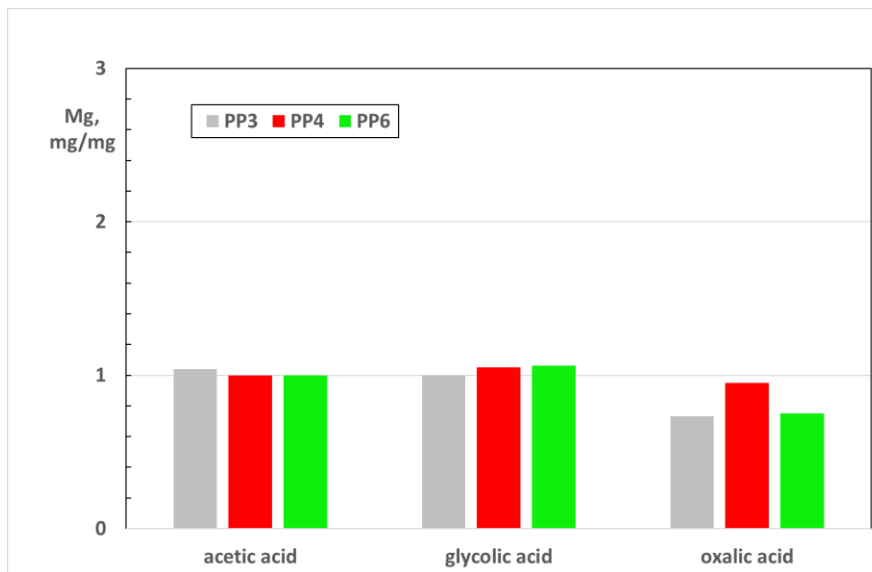
The Al concentrations (Table 6) in the leachates of the rich loaded MEA solutions without any dosage differ significantly from each other for the 3 ESP ashes, from a low level of 0.77 mg/l (PP3) to 25 mg/l (PP6). Considering the normalized data of Al (Figure 23), each acid contributes to a higher concentration level, but quite differently for each ESP ash. The ESP ash of PP4 releases the highest amount of alumina for each added acid.



**Figure 24:** Normalized changes for Ca in the leachates of ESP ashes from different power plants caused by the addition of different acids to the liquid before leaching

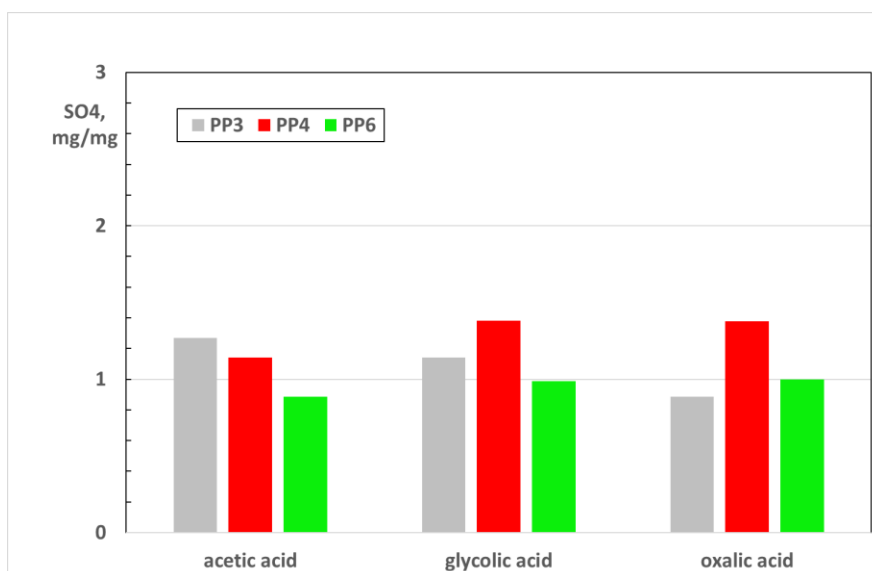
The impact of acetic and glycolic acids on the dissolution of Ca (Figure 24) is low for the ESP ashes of PP3 and PP6, but for PP4 there is a significant increase. Oxalic acid reduces the Ca concentration by around 80 % (Figure 24), on average for the three ESP ashes. It can be assumed that Ca oxalate precipitates in the solution.

The influence of acetic and glycolic acid for Mg (Figure 25) is very low for all three ESP ashes. Oxalic acid reduces the Mg concentration by around 20 % on average for the three ESP ashes.

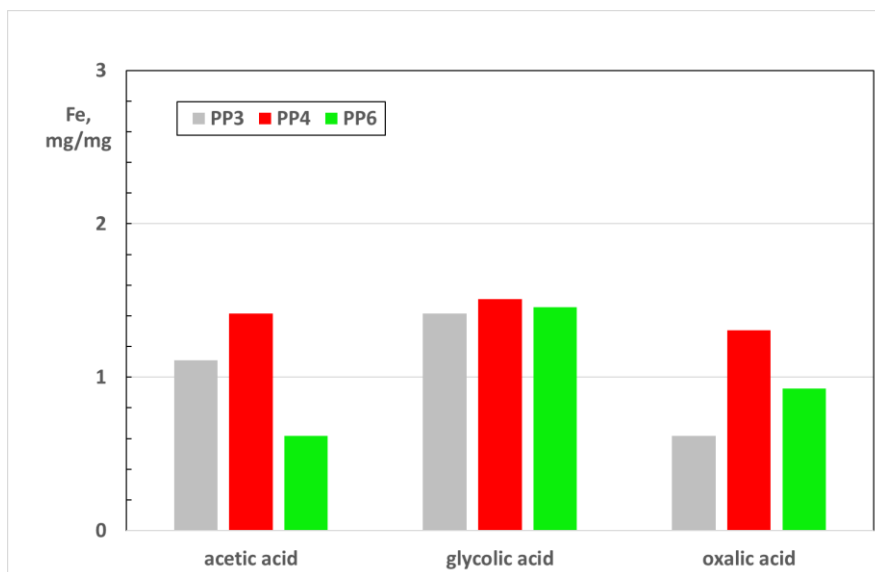


**Figure 25:** Normalized changes for Mg in the leachates of ESP ashes from different power plants caused by the addition of different acids to the liquid before leaching

The sulfate concentrations do not behave uniformly (Figure 26). While the sulfate concentration measured for the ESP ash PP4 generally increases after the addition of different acids to varying degrees, there is no enhancement in terms of the ESP ash PP6. With regard to PP3, the sulfate concentrations either increase (after the addition of acetic and glycolic acids) or decrease (after addition of oxalic acid).

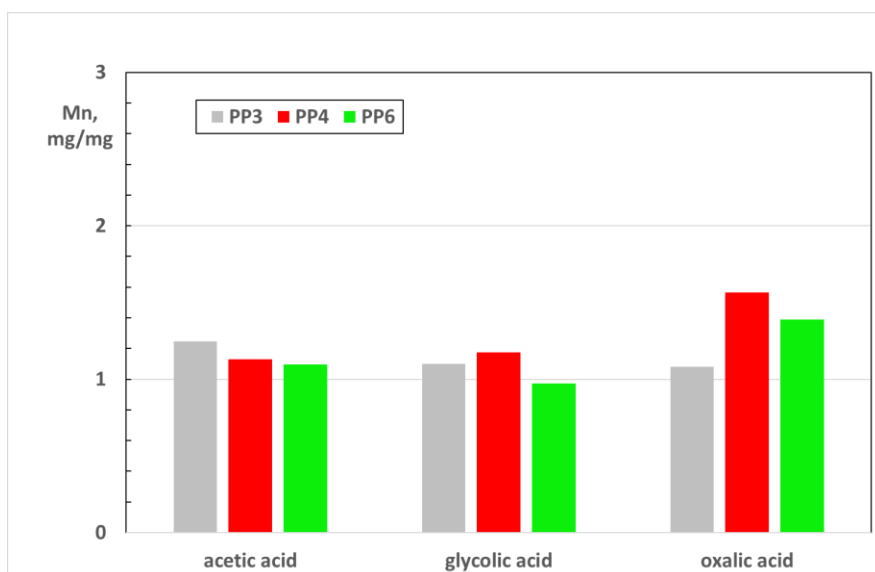


**Figure 26:** Normalized changes for sulfate in the leachates of ESP ashes from different power plants caused by the addition of different acids to the liquid before leaching



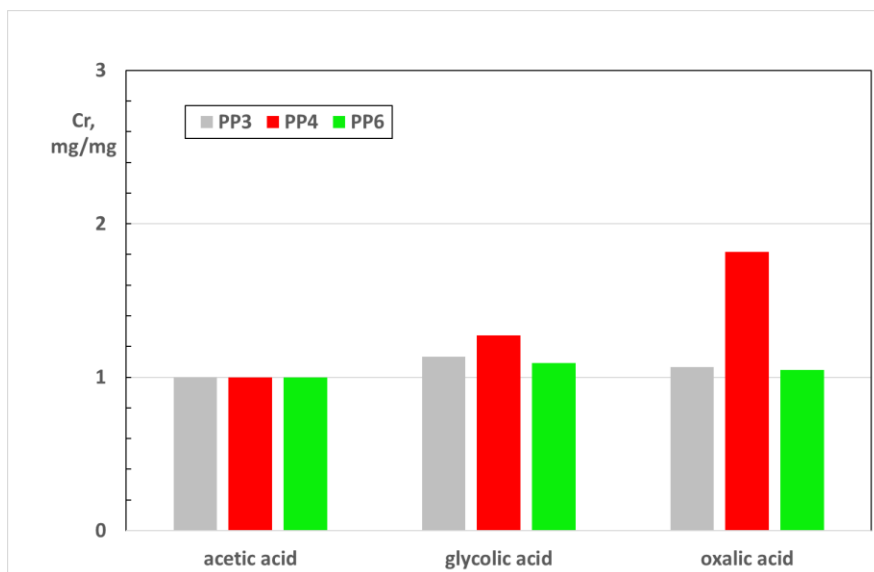
**Figure 27:** Normalized changes for Fe in the leachates of ESP ashes from different power plants caused by the addition of different acids to the liquid before leaching

The behaviour of Fe is also non-uniform (Figure 27). There is an enhancement and a reduction by acetic and oxalic acid. Glycolic acid raises the Fe concentration uniformly for each ESP ash, on average up to 40 %.

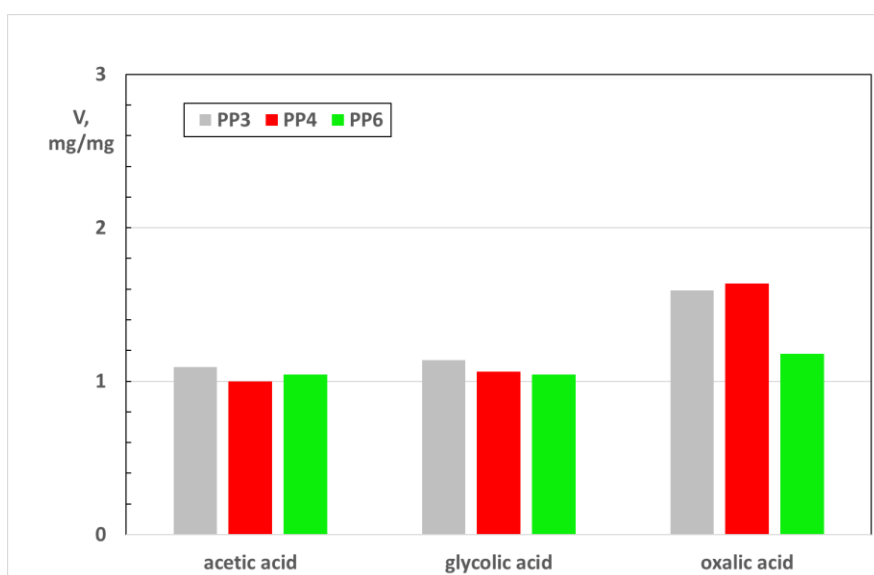


**Figure 28:** Normalized changes for Mn in the leachates of ESP ashes from different power plants caused by the addition of different acids to the liquid before leaching

Mn concentrations (Figure 28) are increased on average to around 15 % by acetic acid, to around 10 % by glycolic acid and to around 35 % by oxalic acid for the three ESP ashes.



**Figure 29:** Normalized changes for Cr in the leachates of ESP ashes from different power plants caused by the addition of different acids to the liquid before leaching



**Figure 30:** Normalized changes for V in the leachates of ESP ashes from different power plants caused by the addition of different acids to the liquid before leaching

The performances of Cr (Figure 29) and V (Figure 30) are similar for acetic and glycolic acid. Acetic acid has no impact on the Cr concentrations and a only a quite small one on the V concentrations. The glycolic acid achieves only an enhancement of the Cr up to 27 % and for V concentrations up to 14 %. The impact of oxalic acid is non-uniform for Cr and V of the three ESP ashes, but significant for the ESP ash PP4. For this ESP ash the Cr concentrations increased by around 80 % and the V concentrations by around 60 %.

This underlines that there could be an enhancement of heavy metal concentrations for some ESP ashes by oxalic acid.

#### **Lessons learned from chapter 4.4**

1. Oxalic acid in the leaching solution releases phosphate from the ESP ashes and precipitates Ca significantly, Mg partly and at times also Fe.
2. Oxalic acid raises the concentrations of V on average by 47 %, Mn on average by 35% and Cr by 31 %.
3. Glycolic acid enhances the Fe concentration for all three ESP ashes uniformly, on average to 40%.
4. The impact of acetic acid is predominantly small compared to glycolic or oxalic acid.
5. The Al concentrations are increased by all three carbonic acids added to the leaching liquid, but non-uniformly.

#### **4.5 Relevance of the solid to liquid ratio**

The following section deals with modifications of the solid to liquid ratio, as this parameter also affects the concentrations of heavy metals in the leachates.

When a CC plant behind a hard coal-fired power station will start operation, the liquid inventory is completely free of fly ash particulate matter. Due to the absorption of fly ash particles inside the CO<sub>2</sub> absorber column as a result of operation, the solid to liquid ratio is never constant and will increase continuously over time. After one hour of operation it could be a solid to liquid ratio of 1:1000000 (g/g), which means 1 mg fly ash per kg of liquid. Such a ratio can hardly be studied under lab scale conditions because of the technical equipment and the limitations of analytical methods. Probably none of the analytical parameters could be detected. Given such a ratio (1:1000000, g/g), the liquid still remains clear, the fly ash particles are homogeneously distributed and must still be taken out by filtration at the end of the leaching time to prevent effects on the analytical result from the leachate.



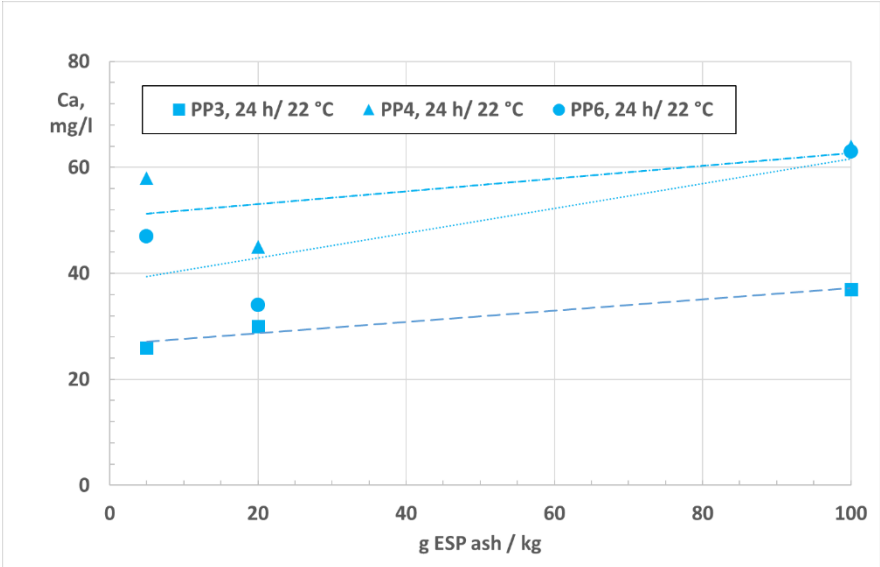
The dependence of the dissolved concentrations on the solid to liquid ratio starts at zero mg/l for each compound or element, if we assume a non-contaminated MEA solution. For a solid to liquid ratio e.g. 1:10 (g/g) saturation for some elements or compounds might occur.

**Table 8:** Analytical results of the leachates based on rich loaded MEA solutions at three solid to liquid ratios and applied for leaching of three ESP ashes; **red values** are LOD values

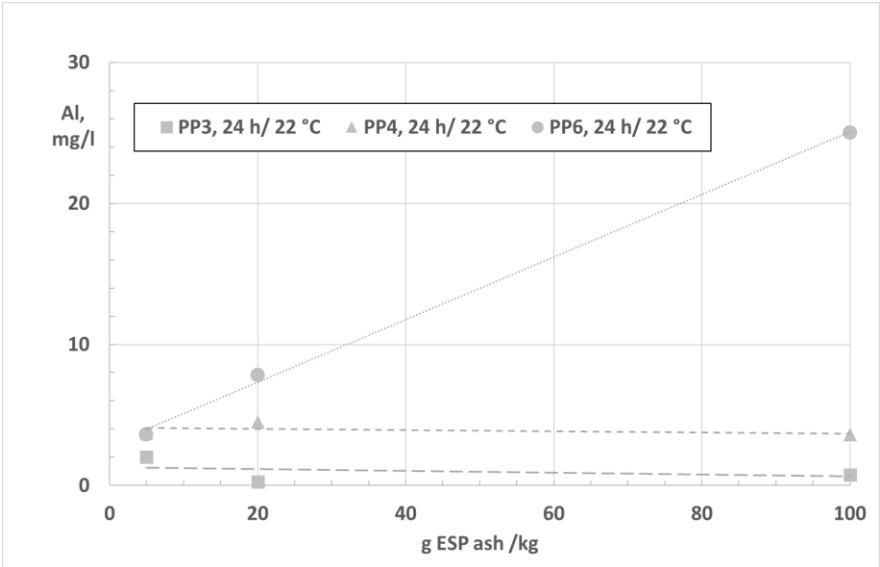
		PP3, 24 h/22 °C			PP4, 24 h/22 °C			PP6, 24 h/22 °C		
		rich 4.4 M MEA			rich 4.3 M MEA			rich 4.3 M MEA		
		1+200	1+50	1+10	1+200	1+50	1+10	1+200	1+50	1+10
	g ESP ash/kg	5	20	100	5	20	100	5	20	100
<b>pH</b>		8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6
<b>conductivity</b>	mS/cm	35.0	35.0	34.4	35.0	35.1	34.0	35	35	35.2
<b>density</b>	g/mL	1.1102	1.1133	1.1156	1.1102	1.1119	1.1152	1.1175	1.1136	1.1143
<b>alkalinity pH 7</b>	meq/kg	2348	2368	2478	2348	2403	2435	2430	2363	2385
<b>alkalinity pH 4</b>	meq/kg	4189	4287	4392	4189	4288	4347	4369	4300	4269
<b>loading</b>	mol/mol	0.44	0.45	0.44	0.44	0.44	0.44	0.44	0.45	0.44
<b>chloride</b>	mg/L	4	2	1	4	2	6	2	2	1
<b>phosphate</b>	mg/L	16	40	110	40	71	212	10	27	86
<b>sulfate</b>	mg/L	25	64	390	25	100	760	33	97	620
<b>formate</b>	mg/L	32	30	38	32	38	35	35	40	38
<b>oxalate</b>	mg/L	5	5	5	5	5	5	5	5	5
<b>Na</b>	mg/L	1.6	5	23	2.4	7.5	35	1.8	6	27
<b>K</b>	mg/L	0.23	1.2	6.8	0.85	3.2	13	0.74	3.3	16
<b>Mg</b>	mg/L	16	56	260	14	46	200	10	36	160
<b>Ca</b>	mg/L	26	30	37	58	45	64	47	34	63
<b>Al</b>	mg/L	2	0.28	0.77	3.7	4.5	3.6	3.6	7.8	25
<b>V</b>	mg/L	0.2	0.57	2.2	0.35	0.86	3.3	0.32	1.0	4.5
<b>Cr</b>	mg/L	0.1	0.37	1.5	0.12	0.34	1.1	0.14	0.52	2.2
<b>Mn</b>	mg/L	0.11	0.19	0.61	0.39	0.97	2.3	0.14	0.34	0.72
<b>Fe</b>	mg/L	9.1	29	99	7	19	55	7.4	25	92
<b>Ni</b>	mg/L	0.05	0.07	0.31	0.05	0.16	0.66	0.05	0.07	0.33
<b>Cu</b>	mg/L	0.05	0.1	0.43	0.2	0.66	2.7	0.05	0.2	0.83

Leaching experiments are performed under room temperature and over 24 hours for three ESP ashes and three solid to liquid ratios. These experiments help evaluate the behaviour of the dissolved elements or compounds at these ash concentrations and extrapolate the concentrations of Fe and other heavy metals to ratios e.g. 1:1000 or 1:10000 (g/g). Table 8 lists all results of these experiments. In spite of quite different solid to liquid ratios the concentrations of Ca do not change significantly (Figure 31). As shown in Figures 31-46, the solid to liquid ratios are used as g ESP ash per kg MEA solution which means e.g. 100 g ESP ash/kg MEA solution for a solid to liquid ratio of 1:10 (g/g). Each ESP ash possesses its own level, each trend is marked by a linear regression line. It is assumed that the low solubility of calcium hydrogenphosphate ( $\text{CaHPO}_4$ ) limits the concentration level of Ca due to saturation. [D'Ans 1943] published a solubility of 140 mg  $\text{CaHPO}_4$  in 1 kg water at 40 °C, which suits the determined concentration levels. The behaviour of Al (Figure 32) is very different for each ESP ash. The Al concentration in the leachate of the ESP ash PP6 increases with rising ESP ash concentration. The trend is marked by straight regression lines. But for the ESP ashes of PP4

and PP3 there is no dependency on the ESP ash concentration that would favour a solubility equilibrium. Most likely this is related to the high phosphate concentrations in the leachates of the rich loaded MEA solutions. AlPO<sub>4</sub> is only slightly soluble in water.



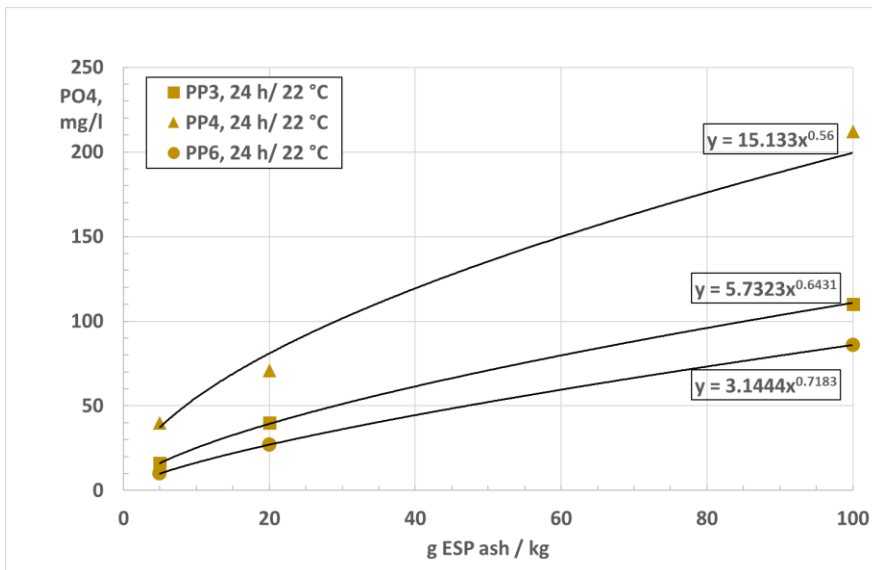
**Figure 31:** Concentrations of Ca in the leachates for ESP ashes from different power plants as a function of the ESP ash concentration in the rich loaded MEA concentration



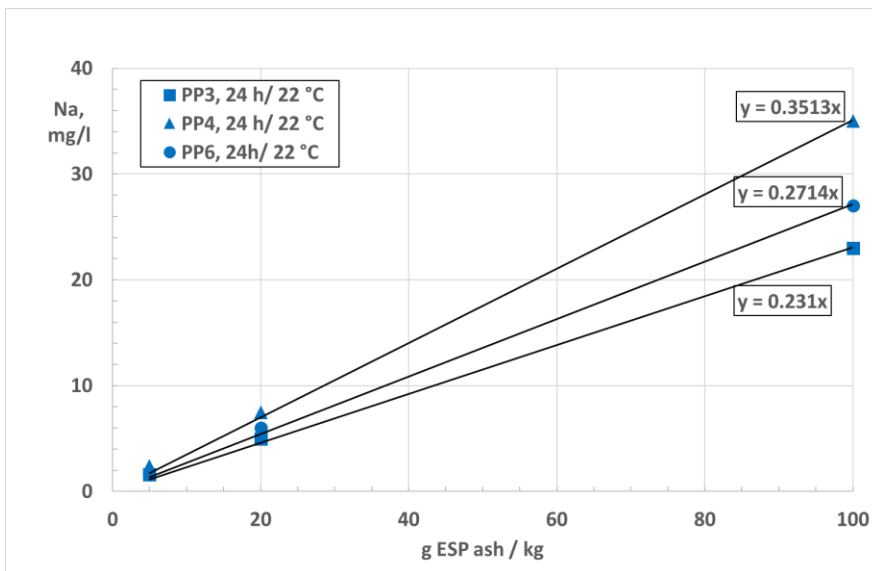
**Figure 32:** Concentrations of Al in the leachates for different ESP ashes as a function of the ESP ash concentration in the rich loaded MEA concentration

The dependency of phosphate itself (Figure 33), which fits a regression curve of a power function, indicates that the solubility is limited at high concentrations. Each ESP ash has its

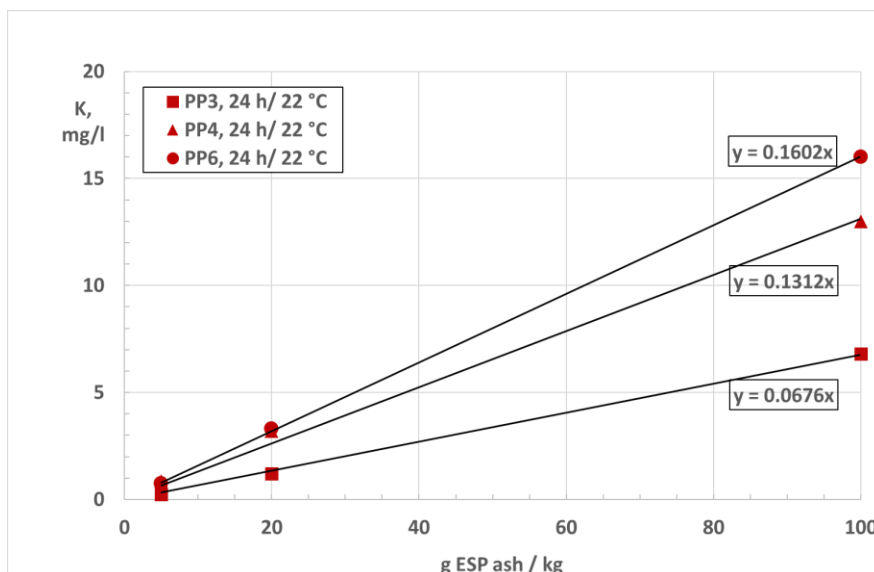
own specific dependency. At low ESP ash concentrations all three dependent concentrations of phosphate are close to zero.



**Figure 33:** Concentrations of phosphate in the leachates for ESP ashes from different power plants as a function of the ESP ash concentration in the rich loaded MEA concentration

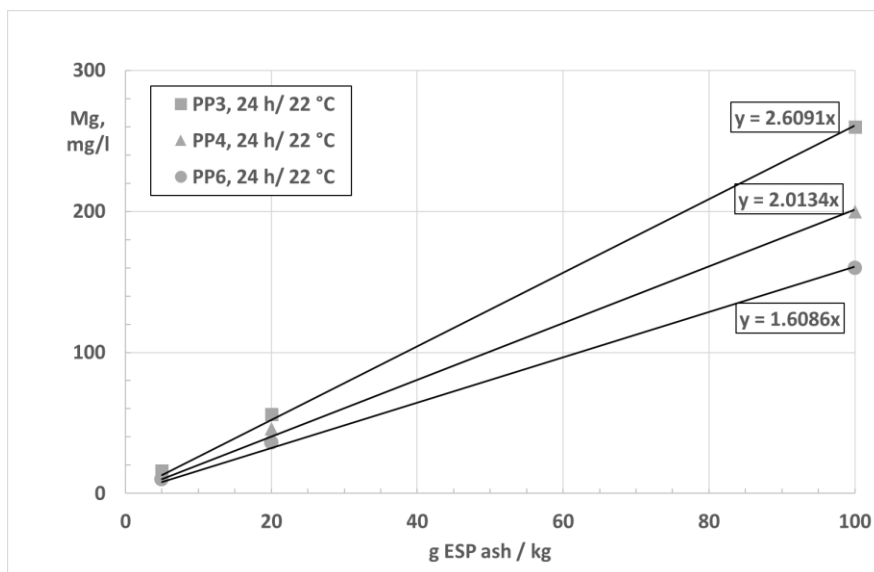


**Figure 34:** Concentrations of Na in the leachates for ESP ashes from different power plants as a function of the ESP ash concentration in the rich loaded MEA concentration

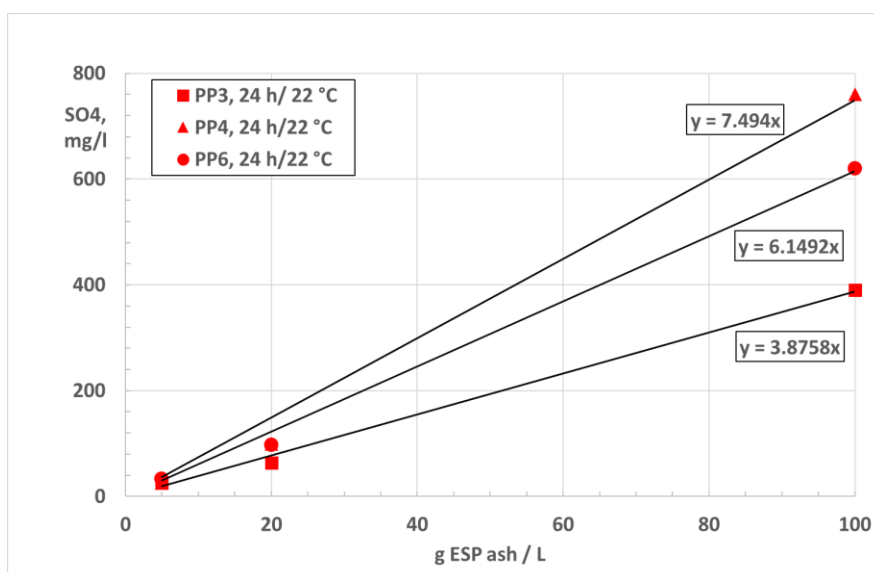


**Figure 35:** Concentrations of K in the leachates for ESP ashes from different power plants as a function of the ESP ash concentration in the rich loaded MEA concentration

Figure 34 shows the linear dependencies for Na and Figure 35 for K. Considering the high solubility of Na and K salts in water, this linear dependency could be expected. The origin is part of the linear regression calculation, as well for the calculations in Figures 31-37. Figure 36 shows the dependencies for Mg and in Figure 37 for sulfate for all ESP ashes. These dependencies differently fit linear regression lines. Magnesium sulfate is one of the salts which is dissolved from the surface of fly ash particles by the rich loaded MEA solution, but the concentration of  $MgSO_4$  is different for each ESP ash. There is also a linear dependency of sulfate to the ESP ash concentration in the rich MEA solution, although the results of sulfate at 20 g ESP ash per kg for all three ESP ashes deviate to lower values. Because all three samples are concerned, it might be an analytical error.

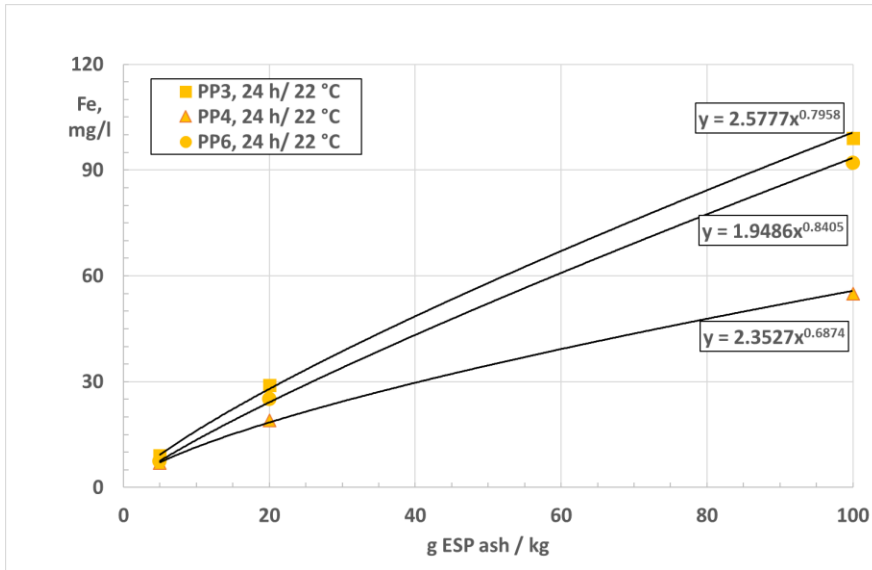


**Figure 36:** Concentrations of Mg in the leachates for different ESP ashes as a function of the ESP ash concentration in the rich loaded MEA concentration



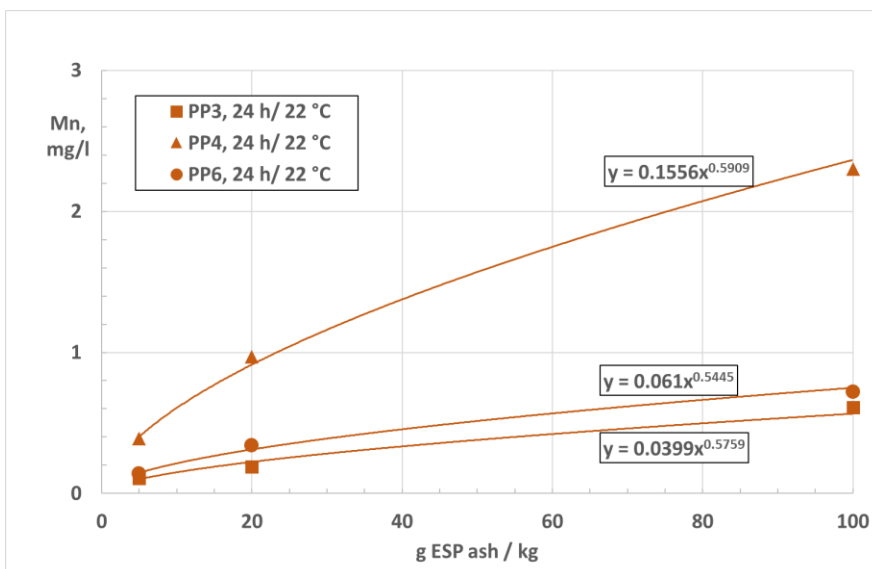
**Figure 37:** Concentrations of sulfate in the leachates for ESP ashes from different power plants as a function of the ESP ash concentration in the rich loaded MEA concentration

The behaviour of Fe (Figure 38) is quite similar to that of phosphate. In the range of 5 to 100 g ESP ash per kg Fe concentrations do not increase linearly, but by a power function. The concentrations of the other heavy metals Mn (Figure 39), V (Figure 40), Cr (Figure 41) and Cu (Figure 42) are analysed for values below 5 mg/l, even at 1:10 (g/g). The Ni concentrations reach just 0.7 mg/l (1:10, g/g) at maximum.

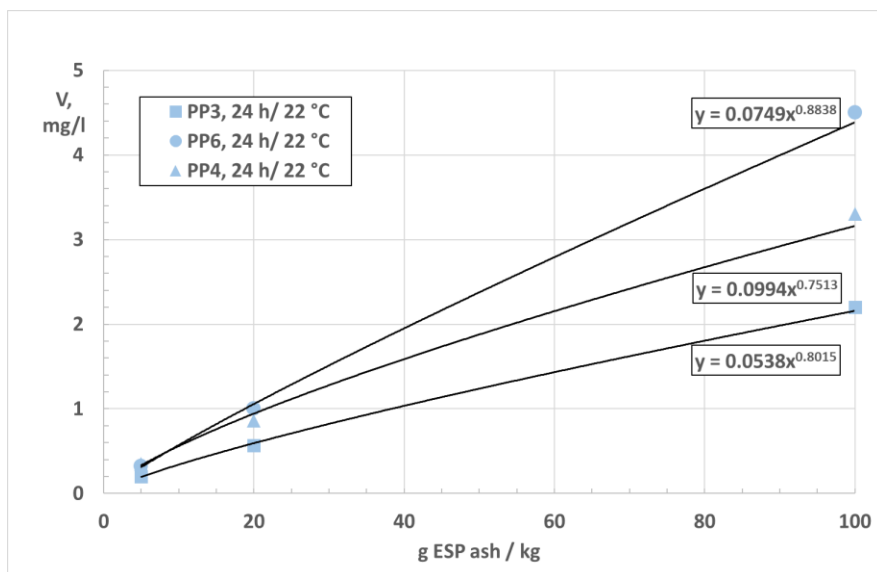


**Figure 38:** Concentrations of Fe in the leachates for different ESP ashes as a function of the ESP ash concentration in the rich loaded MEA concentration

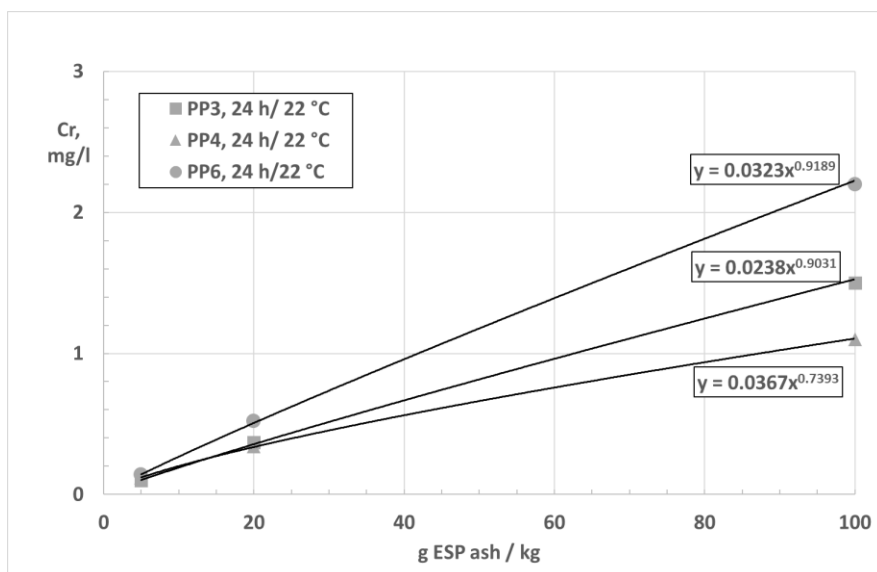
The dependency on the ESP ash concentration is common to all the 4 heavy metals (V, Cr, Mn and Cu). While they all fit a power function, the parameters of these functions vary for each ESP ash and each heavy metal (Figure 39 to Figure 42). The regression curves can be used to estimate the concentration in the leachates for solid to liquid ratios at 1:1000 (1 g/kg) or 1:10000 (100 mg/kg).



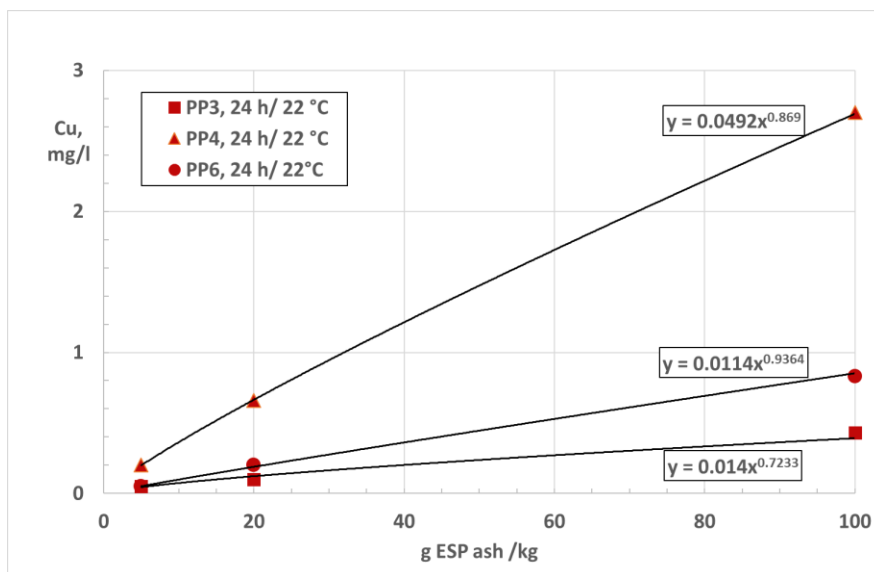
**Figure 39:** Concentrations of Mn in the leachates for ESP ashes from different power plants as a function of the ESP ash concentration in the rich loaded MEA concentration



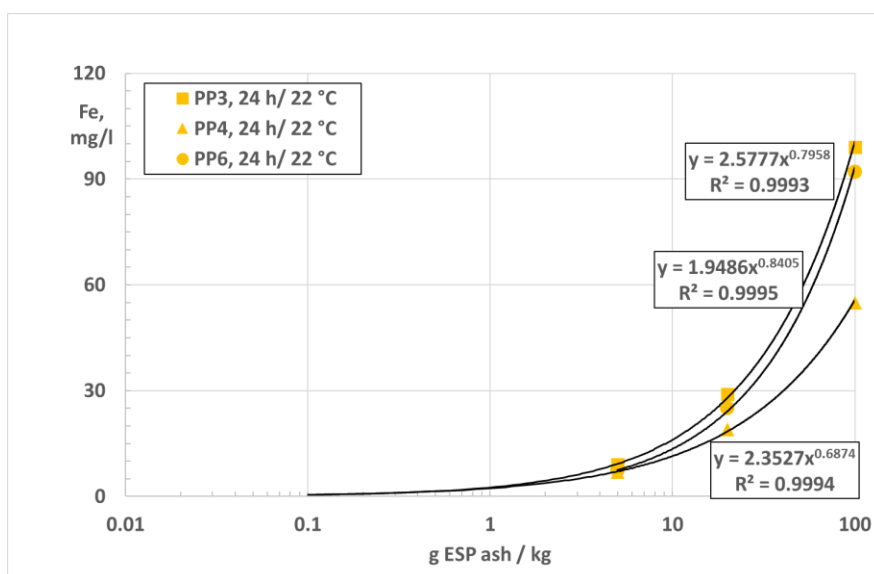
**Figure 40:** Concentrations of V in the leachates for ESP ashes from different power plants as a function of the ESP ash concentration in the rich loaded MEA concentration



**Figure 41:** Concentrations of Cr in the leachates for ESP ashes from different power plants as a function of the ESP ash concentration in the rich loaded MEA concentration



**Figure 42:** Concentrations of Cu in the leachates for ESP ashes from different power plants as a function of the ESP ash concentration in the rich loaded MEA concentration



**Figure 43:** Concentrations of Fe in the leachates for different ESP ashes in dependence of the ESP ash concentration in the rich loaded MEA concentration, log scale

Figure 43 shows the same results of Fe as in Figure 38 with the same regression curves, but using a log scale for the x-axis. At a low solid to liquid ratio of 1:1000 (g/g), the Fe estimated concentrations vary between 2.0 and 2.6 mg/l (0.3-0.5 mg/l at 1:10000, g/g). Given a solid to liquid ratio of 1:100000 (10 mg/kg), the Fe concentrations are estimated to nearly reach the detection limit of 0.05 mg/l. Based on the regression curves of V, Cr, Mn and Cu, the

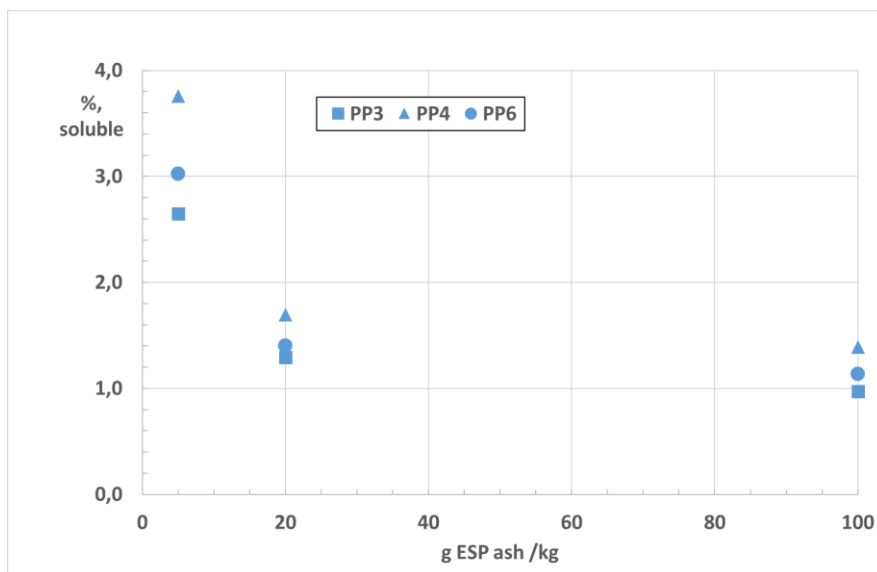


concentration level for the ESP ash of PP4 at 1:1000 (g/g) is predicted to reach 0.16 mg/l at maximum. Given the same ratio, the maximum level for the ESP ashes of PP3 and PP6 amounts to 0.08 mg/l.

Table 9 contains the calculated sum of the dissolved species, neglecting values of the limit of detection. When all dissolved elements and compounds, which were dissolved from the ESP ash, are summed up, then the soluble part of the ESP ash is estimated. This sum is not complete because some elements and compounds are not analysed, but it gives an order of magnitude. The LOD values are not considered. Table 9 lists these sums and shows the converted data to mg/kg ESP ash and % which are dissolved under the leaching condition. The soluble part of the ESP ash increases to lower ESP ash concentration (Figure 44). About 1-1.4 % of the ESP ashes are dissolved at 1:10 (g/g), 22 °C and 24 h. The same tendency is observed when the Fe concentrations are converted to mg Fe dissolved per kg ESP ash (Table 10, Figure 45). The dissolved Fe is equal to about 0.1 % of the ESP ash at 1:10 (g/g), 22 °C and 24 h . Related to the Fe content in the ESP ash, a bandwidth of 1.4-2.2 % soluble Fe is determined at 1:10, g/g (Figure 46). The highest Fe value in the ESP ash does not reveal the highest value in the leachate.

**Table 9:** Sum of the dissolved species in the leachates (Table 8) without LOD values and their conversion to mg/kg and % soluble

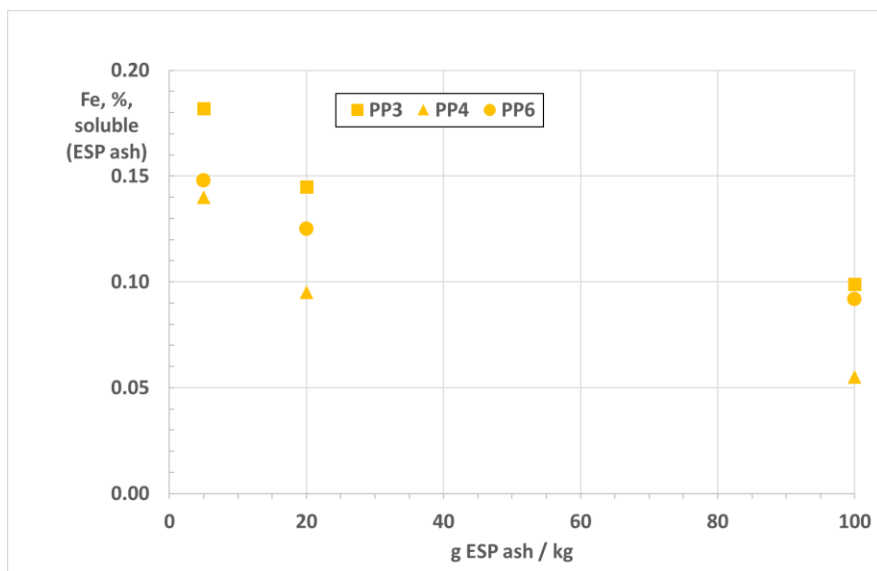
		PP3, 24 h/22 °C			PP4, 24 h/22 °C			PP6, 24 h/22 °C		
		rich 4.4 M MEA			rich 4.3 M MEA			rich 4.3 M MEA		
		1:200	1:50	1:10	1:200	1:50	1:10	1:200	1:50	1:10
g ESP ash/kg		5	20	100	5	20	100	5	20	100
sum w/o LOD	mg/l	132.4	258.8	970.6	188.1	339.2	1393.7	151.1	280.2	1136.6
sum	mg/kg, soluble	26478	12939	9706	37612	16960	13937	30228	14012	11366
sum	%, soluble	2.6	1.3	1.0	3.8	1.7	1.4	3.0	1.4	1.1



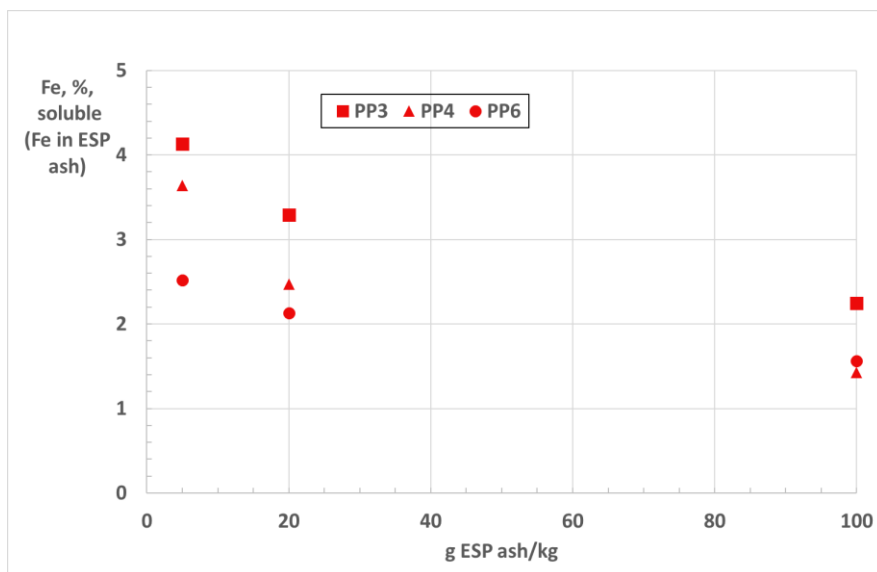
**Figure 44:** Results of the soluble part of the ESP ashes as a function of the solid to liquid ratio

**Table 10:** Dissolved mass of Fe in relation to the ESP ash mass which is leached and the dissolved mass of Fe in relation to the Fe content in the ESP ash

		PP3, 24 h/22 °C rich 4.4 M MEA			PP4, 24 h/22 °C rich 4.3 M MEA			PP6, 24 h/22 °C rich 4.3 M MEA		
		1:200	1:50	1:10	1:200	1:50	1:10	1:200	1:50	1:10
g ESP ash/kg		5	20	100	5	20	100	5	20	100
Fe	mg/l	9.1	29	99	7	19	55	7.4	25	92
Fe	mg/kg ash, soluble	1820	1450	990	1400	950	550	1480	1250	920
Fe	% soluble	0.18	0.15	0.10	0.14	0.10	0.06	0.15	0.13	0.09
Fe <sub>2</sub> O <sub>3</sub> in ESP ash	%	6.3	6.3	6.3	5.5	5.5	5.5	8.4	8.4	8.4
Fe in ESP ash	ppm	44062	44062	44062	38467	38467	38467	58750	58750	58750
Fe	% Fe, soluble	4.1	3.3	2.2	3.6	2.5	1.4	2.5	2.1	1.6



**Figure 45:** Results of soluble Fe regarding the mass ESP ash as a function of the solid to liquid ratio



**Figure 46:** Results of soluble Fe regarding the Fe content in the ESP ash as a function of the solid to liquid ratio

**Table 11:** Ion balance for the analytical results of the leachates based on Table 8 for three solid to liquid ratios; red values are LOD values; \*values of carbonate and hydrogencarbonate added to close the ion balance

	g ESP ash/kg	PP3, 24 h/22 °C rich 4.4 M MEA			PP4, 24 h/22 °C rich 4.3 M MEA			PP6, 24 h/22 °C rich 4.3 M MEA		
		1:200	1:50	1:10	1:200	1:50	1:10	1:200	1:50	1:10
		5	20	100	5	20	100	5	20	100
hydroxide	meq / l	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
chloride	meq / l	0.11	0.06	0.03	0.11	0.06	0.17	0.06	0.06	0.03
phosphate	meq / l	0.34	0.84	2.32	0.84	1.50	4.46	0.21	0.57	1.81
sulfate	meq / l	0.52	1.33	8.13	0.52	2.08	15.83	0.69	2.02	12.92
carb. + hydrogencarb. *	meq / l	2.28	5.25	17.90	3.37	4.14	4.07	3.03	4.28	9.73
sum anions	meq / l	3.3	7.5	28.4	4.9	7.8	24.5	4.0	6.9	24.5
sodium	meq / l	0.07	0.22	1.00	0.10	0.33	1.52	0.08	0.26	1.17
potassium	meq / l	0.01	0.03	0.17	0.02	0.08	0.33	0.02	0.08	0.41
magnesium	meq / l	1.32	4.61	21.4	1.15	3.78	16.45	0.82	2.96	13.2
calcium	meq / l	1.30	1.50	1.85	2.89	2.25	3.19	2.35	1.70	3.14
aluminium	meq / l	0.22	0.03	0.09	0.41	0.50	0.40	0.40	0.87	2.78
vanadium	meq / l	0.02	0.05	0.17	0.03	0.07	0.26	0.03	0.08	0.35
chromium	meq / l	0.01	0.02	0.09	0.01	0.02	0.06	0.01	0.03	0.13
manganese	meq / l	0.01	0.01	0.04	0.03	0.07	0.17	0.01	0.03	0.05
iron	meq / l	0.33	1.04	3.55	0.25	0.68	1.97	0.27	0.90	3.29
nickel	meq / l	0.002	0.002	0.01	0.002	0.01	0.02	0.002	0.002	0.01
copper	meq / l	0.002	0.003	0.01	0.01	0.02	0.09	0.002	0.01	0.03
sum cations	meq / l	3.3	7.5	28.4	4.9	7.8	24.5	4.0	6.9	24.5

The ion balance (Table 11) is not closed, alkalinity of carbonate and hydrogencarbonate is missing for all leachates. The marked row in Table 11 contains the sum of carbonate and hydrogencarbonate concentrations, which is not analysed, but necessary for closing the ion balance. The ESP ashes behave quite differently. For PP4 the missing alkalinity changes only

slightly with the concentration of ESP ash to be leached. In contrast to PP4 the missing alkalinity rises with increasing ESP ash concentration for PP3 and PP6.

#### **Lessons learned from chapter 4.5**

1. Reactions occur in the rich MEA solution during leaching. These reactions stabilize the concentrations of Ca and partly Al and are hardly dependent from the ratio of solid to liquid at low ratios.
2. The concentrations of Na, K, Mg and sulfate in the leachates drop linearly, when the ESP ash concentration is reduced to lower values.
3. Each ESP ash has its own specific pattern for the dissolved heavy metals at low solid to liquid ratios e.g. 1:10 (g/g). For ratios < 1:1000 the dissolved concentrations become quite similar and the specific character of each ESP ash becomes less important.
4. The concentration of Fe can be estimated to around 50 µg/l at a ratio of 1:100000 (g/g), when the ESP ash contains a Fe concentration of 4-6 %.
5. The heavy metals like V, Cr, Mn and Cu will exceed 50 µg/l at a ratio of approx. 1:1000 (g/g), and Ni at 1:200.
6. Fe released from the content of Fe in the fly ash material varies between 1.4 % (PP4) to 2.2 % (PP3) at 1:10 (g/g)/22 °C/24 h.
7. The increase of the soluble ash at lower solid to liquid ratios (Figure 44) as well as the similar behaviour of dissolved Fe (Figures 45 and 46) might indicate a systematic error and should be confirmed by further examinations. These tests should also include a higher total mass of the ESP ash, but at the same solid to liquid ratio, and a lower membrane pore size of 0.2 µm for filtration.

During the operation of a CC plant the main parameters for the dissolving of Fe from absorbed fly ash material include the rich molar MEA concentration and the solid to liquid ratio. Therefore, it is extremely important to limit the fly dust concentration entering the CC absorber. Other parameters such as temperature [Schallert 2013], leaching time [Schallert 2013] and the concentration of degradation products should also be considered, but their impact is significantly smaller.

## 4.6 Results of repeatability measurements

Leaching experiments are performed four times in parallel at three different solid to liquid ratios under room temperature and 24 hours of leaching time with a lean 5 M MEA solution to assure the whole procedure of leaching and analytics. Two new ESP ashes (PP3 sampled at 05.03.2015, PP7 at 20.06.2015) are used, but not in parallel. There was a time difference of four months between these two runs, but the identical equipment for leaching, filtration and analysis is used. The solid to liquid ratios of 1:100, 1:1000 and 1:10000 (g/g) are chosen to evaluate any potential dependency on the ESP ash concentration in the leachate due to the reproducibility measurements, and to produce results at lower ESP ash concentrations.

The tables 12 and 13 show the results of both runs including the statistical data for the average values (av.), the standard deviation (std.) according to n-1 and the variation coefficient (vc). All elements are analysed by ICP-OES.

**Table 12:** Analytical results of the leachates based on lean loaded 5 M MEA solutions at three solid to liquid ratios each with four repeats for the ESP ash PP3; red values are LOD values

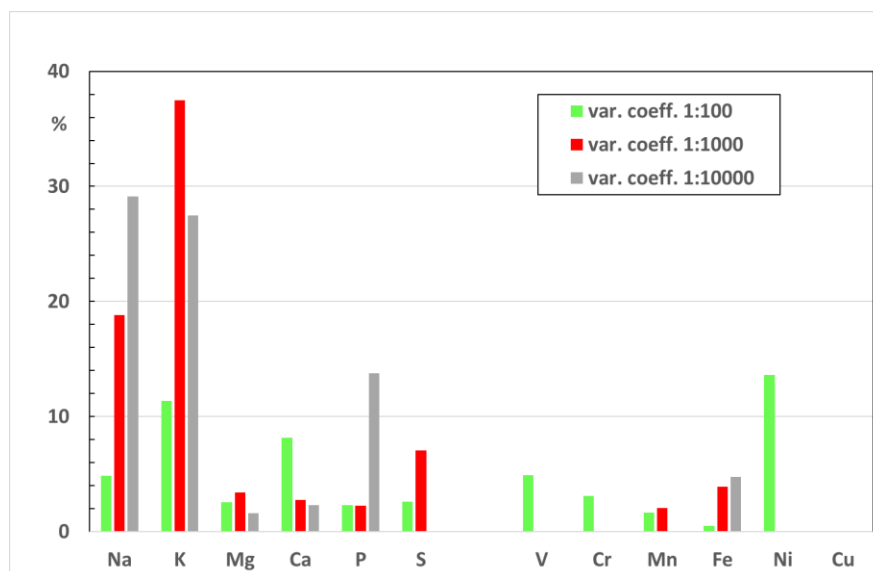
PP3, 05.03.2015																									
	lean 5 M MEA, 24 h/ 22 °C/1:100							lean 5 M MEA, 24 h/ 22 °C/1:1000						lean 5 M MEA, 24 h/ 22 °C/1:10000											
g ESP ash/kg	10	10	10	10				1	1	1	1					0.1	0.1	0.1	0.1						
sample	1	2	3	4	av.	std.	vc	1	2	3	4	av.	std.	vc	1	2	3	4	av.	std.	vc				
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	%	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	%	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	%				
Na	2.0	1.9	1.9	2.1	1.98	0.10	4.8	0.42	0.39	0.31	0.28	0.35	0.07	18.8	0.26	0.3	0.17	0.17	0.23	0.066	29.1				
K	0.85	0.83	0.77	1.00	0.86	0.10	11.3	0.23	0.19	0.11	0.11	0.16	0.06	37.5	0.06	0.09	0.05	0.05	0.06	0.02	27.5				
Mg	19	20	20	20	19.8	0.50	2.5	2.3	2.4	2.5	2.4	2.40	0.08	3.4	0.31	0.32	0.31	0.31	0.31	0.01	1.6				
Ca	53	44	46	47	47.5	3.87	8.2	18	18	19	18	18.25	0.50	2.7	4.2	4.2	4.1	4.0	4.13	0.10	2.3				
P	8.1	8.3	8.5	8.5	8.35	0.19	2.3	2.5	2.5	2.6	2.6	2.55	0.06	2.3	0.33	0.39	0.32	0.28	0.33	0.045	13.8				
S	19	19	20	19	19.3	0.50	2.6	1.9	2.2	2.0	1.9	2.00	0.14	7.1	0.2	0.2	0.2	0.2							
V	0.24	0.26	0.26	0.27	0.26	0.01	4.9	0.05	0.05	0.05	0.05				0.05	0.05	0.05	0.05							
Cr	0.18	0.18	0.19	0.19	0.19	0.01	3.1	0.05	0.05	0.05	0.05				0.05	0.05	0.05	0.05							
Mn	0.35	0.36	0.36	0.35	0.36	0.01	1.6	0.06	0.06	0.06	0.06	0.062	0.00	2.0	0.05	0.05	0.05	0.05							
Fe	9.9	10	10	10	9.98	0.05	0.5	1.2	1.3	1.3	1.3	1.275	0.05	3.9	0.19	0.2	0.21	0.21	0.20	0.01	4.7				
Ni	0.06	0.07	0.06	0.05	0.06	0.01	13.6	0.05	0.05	0.05	0.05				0.05	0.05	0.05	0.05							
Cu	0.1	0.1	0.1	0.1	0.1	0.00	0.0	0.05	0.05	0.05	0.05				0.05	0.05	0.05	0.05							

Figures 47 (PP3) and 48 (PP7) summarize the variation coefficients for the determined parameters. The variation coefficient increases with lower ESP ash concentration of PP3 for K and Na up to approx. 30 % at 0.1 g ESP ash per kg (1:10000). Regarding the main compounds the variation coefficient for P exceeds more than 10 % at 1:10000 (g/g). For the other main elements of the leachate PP3, namely Mg, Ca and S, the variation coefficients are clearly below

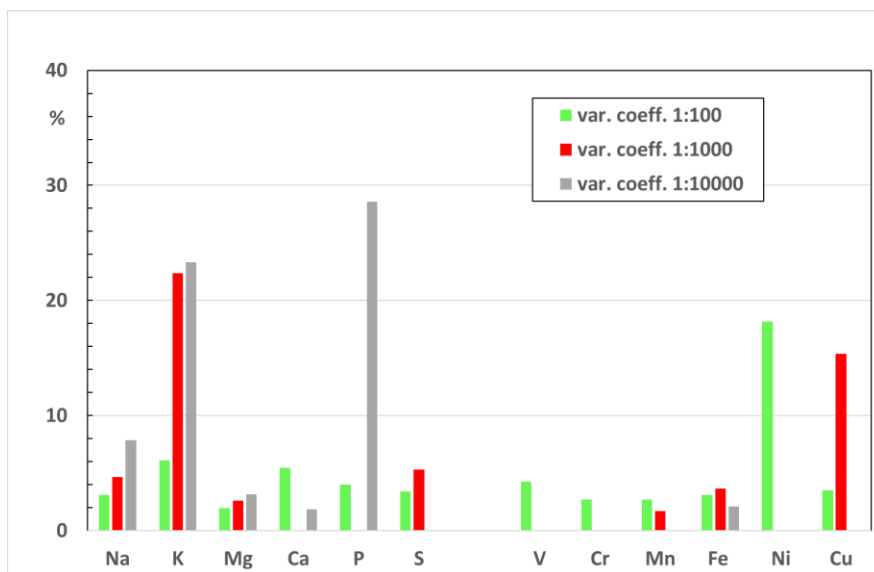
10 % with no dependence to the solid to liquid ratio. Only for Ni, which has the lowest concentration of the determined heavy metals and near to the limit of detection, a variation coefficient above 10 % (Figure 47) is calculated. For the other heavy metals all variation coefficients are below 10 %, when the concentrations have been above their LOD values.

**Table 13:** Analytical results of the leachates based on lean loaded 5 M MEA solutions at three solid to liquid ratios each with four repeats for the ESP ash PP7; red values are LOD values

PP7, 20.06.2015																									
		lean 5 M MEA, 24 h/ 22 °C/1:100						lean 5 M MEA, 24 h/ 22 °C/1:1000						lean 5 M MEA, 24 h/ 22 °C/1:10000											
g ESP ash/kg	10	10	10	10				1	1	1	1					0.1	0.1	0.1	0.1						
sample	1	2	3	4	av.	std.	vc	1	2	3	4	av.	std.	vc	1	2	3	4	av.	std.	vc				
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	%	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	%	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	%				
Na	8.3	8.0	8.1	7.7	8.03	0.25	3.1	1.1	1.1	1.1	1.0	1.08	0.05	4.7	0.29	0.35	0.32	0.31	0.32	0.03	7.9				
K	1.1	1.0	1.1	0.98	1.05	0.06	6.1	0.27	0.21	0.19	0.16	0.21	0.05	22.4	0.05	0.07	0.09	0.07	0.07	0.02	23.3				
Mg	10	9.8	10	9.6	9.85	0.19	1.9	1.9	2	1.9	1.9	1.93	0.05	2.6	0.31	0.31	0.29	0.3	0.30	0.01	3.2				
Ca	71	63	69	65	67.0	3.65	5.4	12	12	12	12	12.0	0.00	0.0	2.8	2.7	2.7	2.7	2.73	0.05	1.8				
P	3.0	2.8	3.0	2.8	2.90	0.12	4.0	1.2	1.2	1.2	1.2	1.20	0.00	0.0	0.2	0.2	0.1	0.2	0.18	0.05	28.6				
S	29	28	29	27	28.3	0.96	3.4	2.7	3	2.9	2.7	2.83	0.15	5.3	1	1	1	1							
V	0.31	0.30	0.30	0.28	0.30	0.01	4.2	0.08	0.08	0.08	0.08	0.080	0.00	0.0	0.02	0.02	0.02	0.02							
Cr	0.22	0.21	0.22	0.21	0.22	0.01	2.7	0.04	0.04	0.04	0.04	0.040	0.00	0.0	0.02	0.02	0.02	0.02							
Mn	0.22	0.21	0.22	0.21	0.22	0.01	2.7	0.03	0.03	0.03	0.03	0.034	0.00	1.7	0.02	0.02	0.02	0.02							
Fe	10	9.6	9.8	9.3	9.68	0.30	3.1	1.3	1.4	1.4	1.4	1.38	0.05	3.6	0.24	0.23	0.24	0.24	0.24	0.005	2.1				
Ni	0.03	0.03	0.03	0.02	0.03	0.01	18.2	0.02	0.02	0.02	0.02				0.02	0.02	0.02	0.02							
Cu	0.17	0.16	0.17	0.16	0.17	0.01	3.5	0.03	0.03	0.04	0.03	0.033	0.01	15.4	0.02	0.02	0.02	0.02							



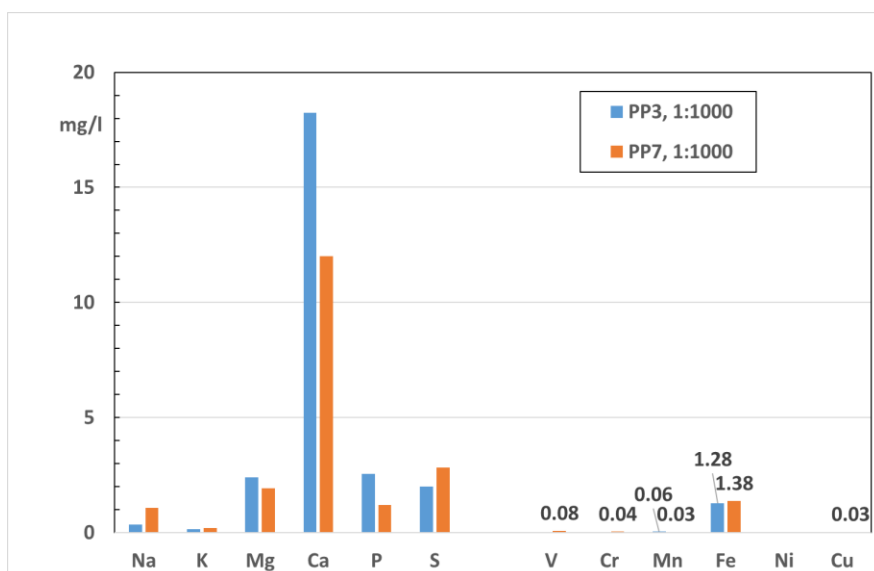
**Figure 47:** Variation coefficient results of four repetitions for all analysed elements and three solid to liquid ratios based on the leaching of the ESP ash PP3 under 22 °C/24 h



**Figure 48:** Variation coefficient results of four repetitions for all analysed elements and three solid to liquid ratios based on the leaching of the ESP ash PP7 under 22 °C/24 h

The results for the ESP ash of PP7 (Table 13, Figure 48) completely deviate from those of PP3, but in principle the behaviour of K, Na, P and Ni is similar. Additionally, the concentrations of Cu are slightly above the detection limit at 1:100 and 1:1000 (g/g), but with increasing variation coefficients according to the very low concentrations.

The variation coefficients for Mg, Ca, S, partly P, V, Cr, Mn, Fe confirm that at least the dependencies of the solid to liquid ratio up to 1:10000 (g/g) can be evaluated confidently.



**Figure 49:** Average values in leachates of PP3 and PP7 at 1:1000 (g/g) and 22 °C/24 h

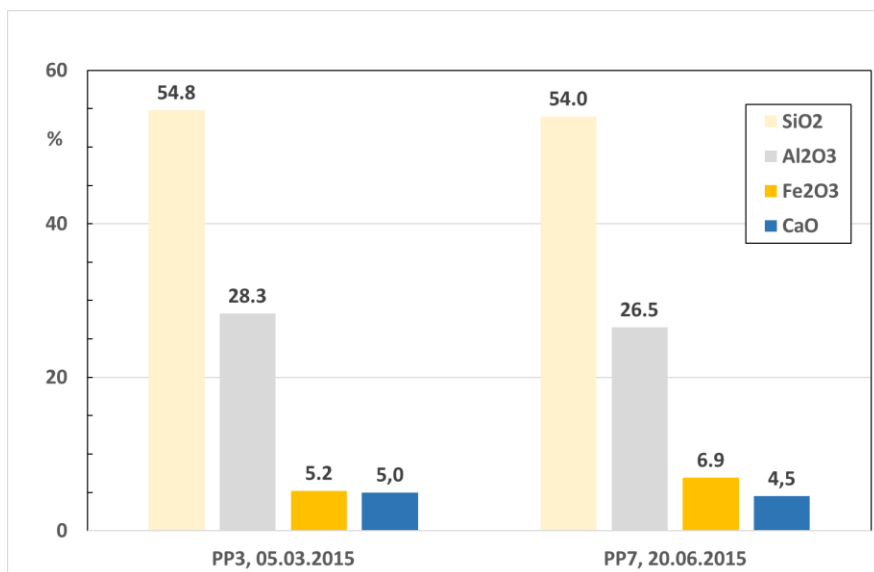
The average values for all detected elements in the leachates of both ESP ashes at a ratio of 1:1000 (g/g) are shown in Figure 49. The main elements Na, Ca and P and for the heavy metals except of Fe strongly differ. These differences relates to the composition of the burnt hard coal and the impact of the firing conditions.

**Table 14:** Main element concentrations of ESP ashes from two different power stations, measured by XRF and calculated as oxides, carbon free

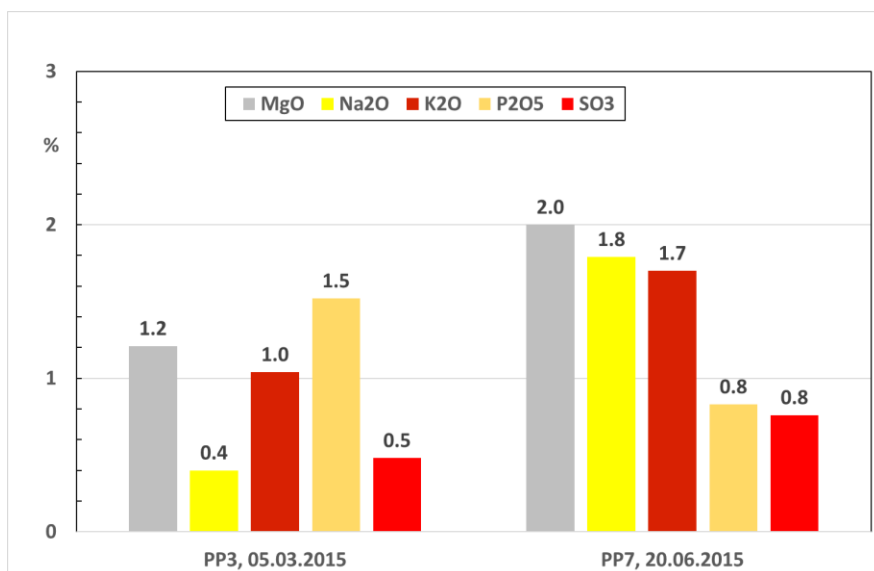
	sampling	PP3	PP7	average
		05.03.2015	20.06.2015	
<b>SiO<sub>2</sub></b>	%	54.8	54.0	54.4
<b>Al<sub>2</sub>O<sub>3</sub></b>	%	28.3	26.5	27.4
<b>Fe<sub>2</sub>O<sub>3</sub></b>	%	5.2	6.9	6.1
<b>TiO<sub>2</sub></b>	%	1.7	1.2	1.4
<b>MgO</b>	%	1.2	2.0	1.6
<b>CaO</b>	%	5.0	4.5	4.8
<b>SrO</b>	%	0.2	0.2	0.2
<b>BaO</b>	%	0.2	0.4	0.3
<b>Na<sub>2</sub>O</b>	%	0.4	1.8	1.1
<b>K<sub>2</sub>O</b>	%	1.0	1.7	1.4
<b>P<sub>2</sub>O<sub>5</sub></b>	%	1.5	0.8	1.2
<b>SO<sub>3</sub></b>	%	0.5	0.8	0.6

Table 14 shows the composition of the ESP ashes for the main compounds. The results of the ESP ash PP3 were published by [Schallert 2016], because other tests were performed regarding the leachability of this ESP ash. In Figure 50 and 51 these main compounds are compared as bar charts and Figure 52 illustrates the comparison of the heavy metals. 33 % more Fe in the ESP ash of PP7 results in 8 % higher Fe concentration in the leachate of PP7 at a solid to liquid ratio of 1:1000 (g/g). But for a quantitative relationship between the element concentration in the ESP ash and the element concentration in the leachate for the main compounds of Table 14 more data (samples and analyses) are needed.



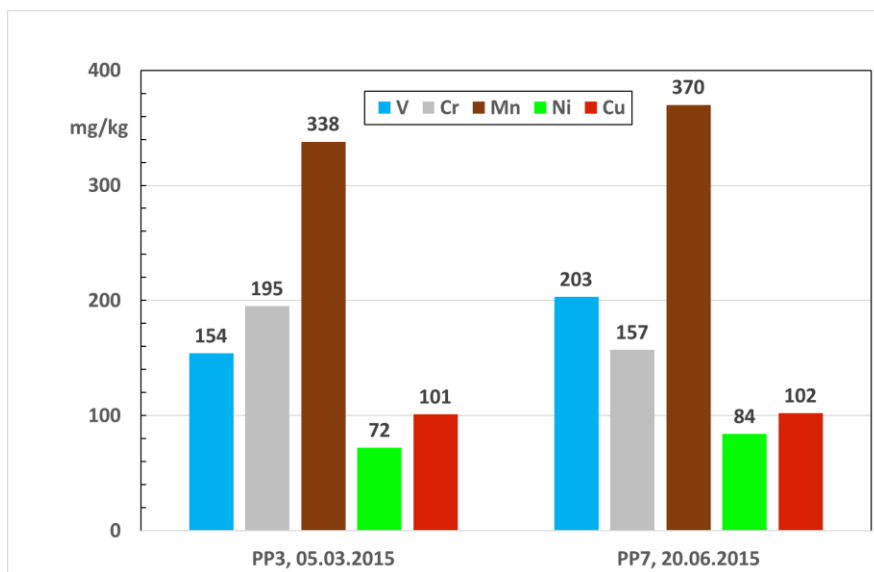


**Figure 50:** Composition of the two studied ESP ashes according to four main compounds



**Figure 51** Composition of the two studied ESP ashes according to the next five main compounds

When the results of the leachates for the heavy metals (Table 12 and 13) are compared to the concentrations in the ESP ashes (fig. 52), no common tendency can be determined. More V in the ESP ash results in a higher concentration in the leachate, but for Mn it is just the opposite. The concentrations for Cu and Cr are too close to the LOD value for a reliable evaluation.



**Figure 52:** Composition of the two studied ESP ashes according to their heavy metals aside to Fe

The results of Table 12 and 13 are very valuable because of an easy application to a lower solid to liquid ratio, e.g. 1:1000.000 (g/g), just assuming a linear dependency and changing the dimension from mg/l to  $\mu\text{g/l}$ . Thus the Fe concentration is estimated to be 1.3-1.4  $\mu\text{g/l}$ , when 1 mg/l of fly ash will be accumulated in the lean 5 M MEA solution.

#### **Lessons learned from chapter 4.6**

1. The repeatability values confirm previous results for Mg, Ca, S, Fe, V, Cr and Mn.
2. The variation coefficients for Na, K and partly P indicate that the analytical tool or the sampling from the ESP ash sample must be revised especially for low concentrations of ESP ash in the leachate.
3. The results for Fe at 1:1000 (g/g) are lower by a factor of approx. 2 compared to the extrapolated results from chapter 4.5, but it should be considered that a lean 5 M MEA has been used for leaching of these 2 ESP ashes instead of a rich 5 M MEA and 2 other ESP ash samples have been leached.
4. At a solid to liquid ratio of 1:10000 (100 mg/kg) only Fe apart from the main elements or compounds could be detected based on a LOD of 0.02 mg/l.
5. The leachate results at 1:1000 are the best available data for further extrapolation, especially the data of PP7.

## 4.7 Prognosis of fly ash and dissolved Fe accumulation

To forecast the liquid concentrations under constant operating conditions for the important parameters as Fe, V, Cr, Mn, Ni and Cu as a function of operating time is a subject of some parameters [Schallert 2016]:

- Flue gas quantity to be treated in  $\text{m}^3/\text{h}$  (STP, dry, 6 %  $\text{O}_2$ ) at the inlet of the absorber
- Liquid inventory  $I_{\text{inv}}$
- Fly dust concentration in  $\text{mg}/\text{m}^3$  (STP, dry, 6 %  $\text{O}_2$ ) at the inlet of the absorber
- Efficiency of the dust removal of the absorber

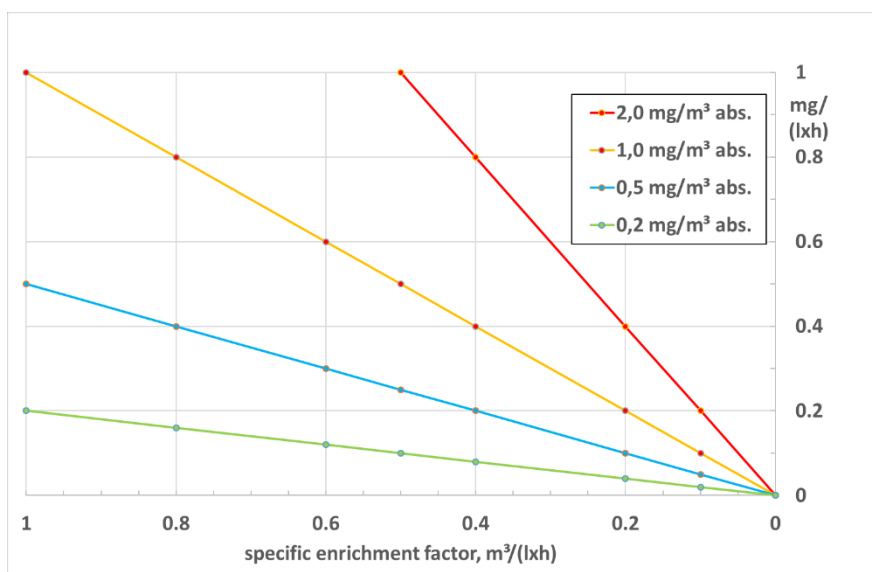
If the ratio of the flue gas flow to the liquid inventory is fixed for a CC plant, then this ratio, named specific enrichment factor (sEF) [Schallert 2016], allows easy calculations under constant operating conditions. The lower this specific enrichment factor will be, the higher the costs are for the sump volumes and the lengths of the liquid lines. Typical values for CC pilot plants are between 0.16 to 0.5  $\text{m}^3/(I_{\text{inv}}*\text{h})$  [Schallert 2016]. No data are yet published for a demonstration plant, but it can be expected that this specific enrichment factor will be higher than 0.5  $\text{m}^3/(I_{\text{inv}}*\text{h})$ , probably around 0.7-0.8  $\text{m}^3/(I_{\text{inv}}*\text{h})$  based on 5 M MEA solution. In order to calculate the specific load in  $\text{mg}/(I*\text{h})$ , the concentration of fly dust and the efficiency of dust removal must be known or assumed. Taking into account 1  $\text{mg}/\text{m}^3$  (STP, dry, 6 %  $\text{O}_2$ ) as the concentration being absorbed into the liquid inventory, then an average fly dust concentration of 1000  $\text{mg}/\text{l}$  in the leachate will be reached after 1250 operating hours under constant operating conditions for a specific enrichment factor of 0.8  $\text{m}^3/(I_{\text{inv}}*\text{h})$ . For this theoretical consideration the time dependency is linear. If the operating conditions for the fly dust concentration upstream the absorber are not constant, which is normal for power plant operation, then deviations from the linearity occur with regard to the following factors:

- Change of coal ash concentration affecting the mass flow of the fly ash
- Variation of the coal composition impacting the efficiency of the ESP
- Load of the power plant decreasing the flue gas velocity and influencing the ESP efficiency
- Sootblowing of the boiler increasing the fly ash concentration during the time of blowing
- Change of the liquid to gas ratio in the FGD biasing the fly ash removal

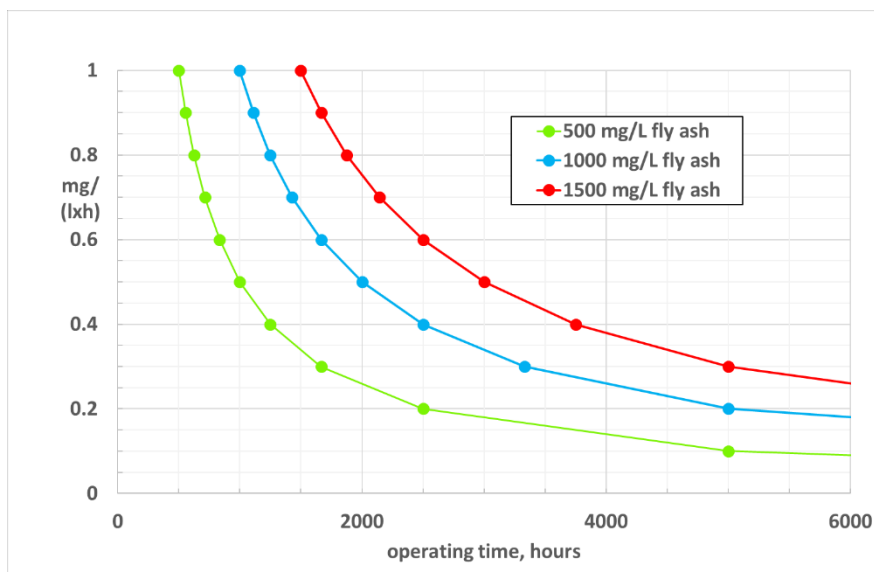
An increase of fly dust concentration for a short time, e.g. in the time of sootblowing, is just a parallel shift of the straight line, a higher concentration being absorbed causes a higher load in  $\text{mg}/(\text{l} \cdot \text{h})$ .

What does this accumulated fly dust concentration mean for Fe and the other heavy metal concentrations in the lean solution? This question cannot be answered for fly dust being absorbed because leaching data are not yet published, but for fly ash based on the leaching results of ESP ash it is possible. [Meij 1994] published that around 40 % of the fly dust is fly ash, the other around 60 % are concerned to gypsum, crystal water and dried salts from droplets leaving the FGD. For the estimation within this study the fly dust concentration is now assumed to be 100 % fly ash, which takes into consideration that the gypsum and the salts might also contribute to the concentration level of Fe and of the other heavy metals in the leachate.

Figure 53 shows the dependency of the load in  $\text{mg}/(\text{l} \cdot \text{h})$  on the specific enrichment factor for different fly ash concentrations being absorbed. Figure 54 points out how much time is necessary to gain a distinct concentration of absorbed fly ash depending on the load in  $\text{mg}/(\text{l} \cdot \text{h})$ . Loads higher than  $0.2 \text{ mg}/(\text{l} \cdot \text{h})$  lead to quite short periods of operation until an averaged concentration of accumulated fly ash e.g.  $1000 \text{ mg}/\text{l}$  is reached.



**Figure 53:** The load of absorbed fly ash in  $\text{mg}/(\text{l} \cdot \text{h})$  as a function of the specific enrichment factor in  $\text{m}^3/(\text{l}_{\text{inv}} \cdot \text{h})$  for different fly ash concentrations being absorbed



**Figure 54:** The load of absorbed fly ash in mg/(l\*h) as a function of the operating time for three fly ash concentrations being accumulated

[Schallert 2016] studied the impact of different residence times of two ESP ash samples on the leachate result is when the total mass of ESP ash is the same. The conclusion was that the ash concentration of the lean solution is more important for the concentration of the dissolved species than the time during accumulation [Schallert 2016]. Therefore, ash concentration values can be converted to species concentrations for an estimation, using leaching results at a solid to liquid ratio near to the ash concentration to be considered e.g. 1:1000 (g/g).

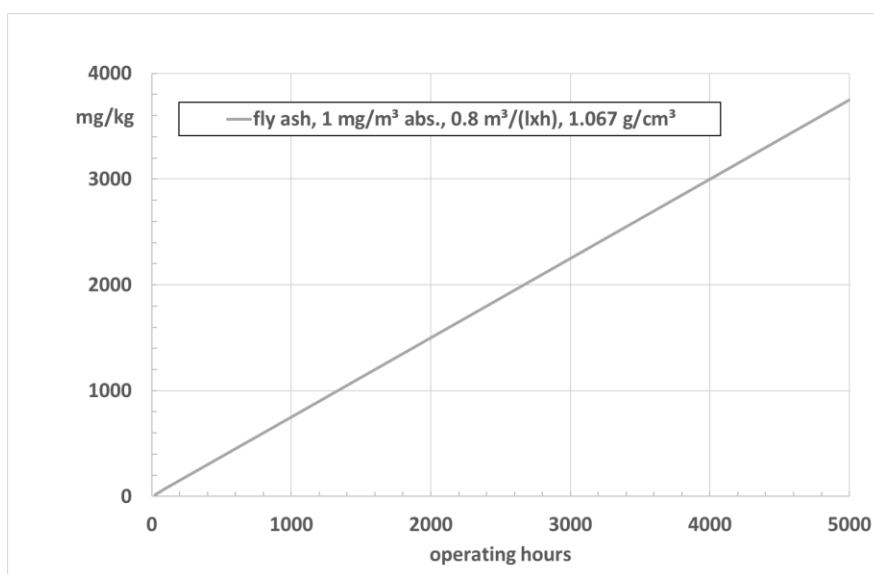
To forecast the Fe concentration as a function of the operating time under constant conditions, model calculations are performed at first according to the time development for the absorbed fly ash of 1 mg/m<sup>3</sup>, considering the specific enrichment factor of 0.8 m<sup>3</sup> / (l<sub>inv</sub>\*h) and the density of the lean 5 M MEA solution (Table 15). Secondly the fly ash concentration in mg/kg (Table 15) is converted to the concentrations of Fe and the other heavy metals using the averaged leachate results at 1:1000 (100 mg fly ash per kg lean 5 M MEA) for PP7 (Table 13). These calculations are based on linear relationships for the accumulated fly ash by time and also for the leached Fe and heavy metal concentrations by time, both starting at zero.

The fly ash concentration in the lean 5 M MEA solution after 24 h is calculated to 18 mg/kg which dissolves 0.025 mg/l Fe. The calculated values for the other heavy metals are far below the limit of detection of 0.02 mg/l. After 1000 hours (Figure 55) the fly ash concentration will

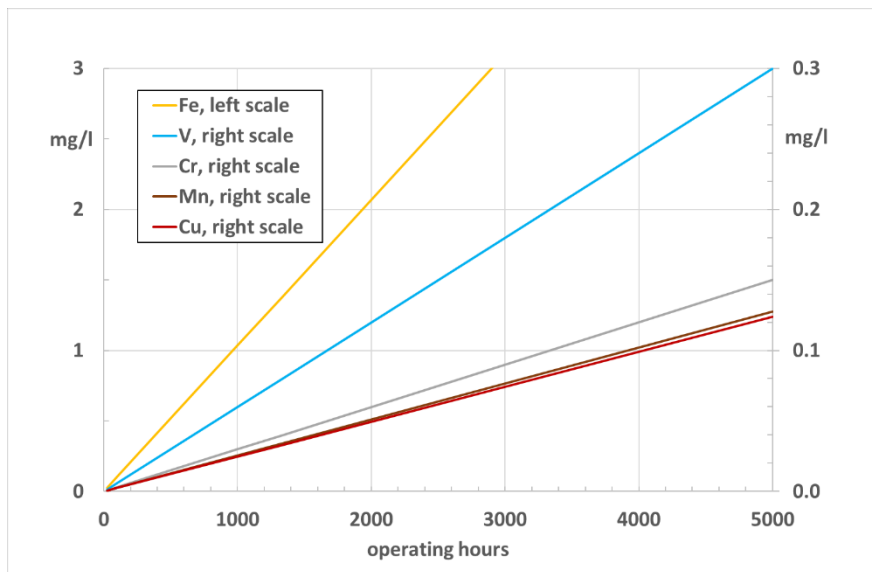
be at around 750 mg/kg, the Fe concentration (Figure 56) at 1.04 mg/l (around 19  $\mu\text{mol/l}$  ( $\mu\text{M}$ ) Fe), the V concentration at 0.06 mg/l, the Cr concentration at 0.03 mg/l, the Mn concentration at 0.03 mg/l and the Cu concentration at 0.03 mg/l (around 0.5  $\mu\text{M}$  Cu).

**Table 15:** Model calculations based on the absorption of 1 mg/m<sup>3</sup>, an enrichment factor of 0.8 m<sup>3</sup>/(l<sub>inv</sub>\*h) and a lean 5 M MEA density of 1.067 g/cm<sup>3</sup> and converted to concentrations for Fe and the other heavy metals using the average values of PP7 at 1:1000 (g/g) (Table 13)

hours	fly ash mg/kg	Fe mg/l	V mg/l	Cr mg/l	Mn mg/l	Cu mg/l
24	18	0.025	0.0014	0.0007	0.0006	0.0006
100	75	0.103	0.006	0.003	0.003	0.002
1000	750	1.035	0.060	0.030	0.025	0.025
1333	1000	1.380	0.080	0.040	0.034	0.033



**Figure 55:** Model calculations for the accumulated fly ash concentration in the lean 5 M MEA solution based on the absorption of 1 mg/m<sup>3</sup> fly ash, an enrichment factor of 0.8 m<sup>3</sup>/(l<sub>inv</sub>\*h) and a lean 5 M MEA density of 1.067 g/cm<sup>3</sup>



**Figure 56:** Model calculations for the dissolved heavy metal concentrations in the 5 M MEA solution based on the absorption of 1 mg/m<sup>3</sup> fly ash, an enrichment factor of 0.8 m<sup>3</sup>/(I<sub>inv</sub>\*h) and a lean 5 M MEA density of 1.067 g/cm<sup>3</sup> and converted to concentrations for Fe and the other heavy metals using the average values of PP7 at 1:1000, g/g (Table 13)

#### **Lessons learned from chapter 4.7**

1. Apart from the main elements such as Ca, Mg and S, only Fe will be detected in the lean 5 M MEA solution of a CC plant after 24 hours of operation when 1 mg /m<sup>3</sup> of fly ash are absorbed by the circulating liquid and a specific enrichment factor of 0.8 m<sup>3</sup>/(I<sub>inv</sub>\*h) is applied. These and the following calculations are based on the leaching results at 1:1000 (g/g)/22 °C/24 h for the ESP ash PP7.
2. Fe concentrations in µg/l will occur in the lean 5 M MEA solution as a function of the operational time due to the leaching of absorbed fly ash particulate matter from the flue gas of a coal-fired power station.
3. The concentration of Fe leached from the absorbed fly ash particulate matter is postulated to linearly increase from the start-up of the CC operation.
4. Fe concentrations above 1 mg/l within the first hundred hours of operation can only be induced by the leaching of fly ash when the absorption of fly ash is at least ten times higher, considering a sEF of 0.8 m<sup>3</sup>/(I<sub>inv</sub>\*h). For a CC plant with a sEF of 0.16 m<sup>3</sup>/(I<sub>inv</sub>\*h) it must be even fifty times higher.

5. The other heavy metals V, Cr, Mn and Cu will be detected predominantly after 350 hours of operation when  $1 \text{ mg/m}^3$  fly ash particulate is absorbed and a specific enrichment factor of  $0.8 \text{ m}^3/(\text{l}_{\text{inv}} \cdot \text{h})$  is applied.
6. When similar concentrations of Fe, Cr and Ni (e.g. all approx.  $1 \text{ mg/l}$ ) occur in the lean 5 M MEA solution, then the leaching of fly ash cannot be the main source because MEA does not leach Ni intensively, but as well not Cr to the same extent as Fe. The corrosion of e.g. the stainless steel material might cause similar concentration levels of Fe, Cr and Ni.



## **5 Discussion of the results**

This chapter mainly focuses on the results of the behaviour of Fe and of directly related parameters. The results are discussed and compared to published data and suggestions are made for further development.

### **5.1 ESP ash composition**

This study investigated ESP ashes with different CaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub> and various heavy metal concentrations in order to determine various concentrations in the leachates. It is yet not possible to confirm that a quite similar composition of the ESP ash will result in a similar leachate composition because other chemical properties like the free lime content and the condensed sulfuric acid may also affect the ESP ash material. Additionally, physical properties like the particle size distribution of the ESP ash material and the related specific surface area are also to be considered. It is yet possible to predict an order of magnitude for the concentration of Fe in a rich loaded 5 M MEA solution at a solid to liquid ratio of 1:1000 (1 g/kg). To forecast the concentrations of the other studied heavy metals at such a ratio is much more difficult because these elements do not behave similarly and the concentration levels of the other heavy metals in the ESP ashes differ quite a lot.

### **5.2 Comparison of the leachates from different liquids for leaching**

To leach ESP ashes with different liquids significantly improves our understanding of ESP ash properties and of reactions that occur in demineralized water, but not in MEA solutions and vice versa. When other solvents are proposed to substitute MEA, for instance because of a smaller energy demand for regeneration, then as well three solutions (demineralized water, non-loaded and rich loaded amine solution) are recommended for leaching in order to find out how this solvent will behave with regard to the absorbed fly ash material.

The leachates of demineralized water contain less than 0.1 mg/l Fe, which is lower than the average values of [Querol 2000] and [Moreno 2005]. Even when at the early beginning of leaching there has been dissolution of a small amount of sulfuric acid from the ESP ash of PP4 causing a short acid drop, the pH value climbed to 9.5 after 24 hours and the precipitation of Fe-hydroxides occurred.  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  possess a very low solubility in water under alkaline conditions ([Stumm 1961] and [Sigg 2011]). The non-loaded 5 M MEA solution dissolves much more Fe compared to demineralized water, but each ESP ash reacts differently. Thus the Fe concentrations vary between 0.7 and 22 mg/l, which is a big bandwidth. By keeping Fe, predominantly as  $\text{Fe}^{2+}$ , in solution within the non-loaded MEA,  $\text{Fe}^{2+}$  must be probably complex bounded to gain Gibbs free energy. This could happen using the free electron pair of the amine group of the MEA molecule in the solution. The much higher concentration of Fe in the rich loaded MEA solutions, in spite of the bandwidth of Fe in the different ESP ashes, indicates that the complexes in the rich MEA solution are even stronger compared to the non-loaded MEA. The dominant ligand of the rich MEA solution is supposed to be the negatively charged MEA carbamate ion with a concentration of around 1.9 mol/l in the leachate. No publication yet focuses on data of MEA carbamate complexes. However, there is no MEA carbamate standard available that can be used for systematic studies. From laboratory studies [McIntosh 1992] it is known that Fe and Mn can be recovered from steel slags by leaching with high concentrated ammonium carbamate solutions at ambient temperature. This process uses the complex bounded iron and manganese for extraction. But a pretreatment at approx. 700 °C using hydrogen for the reduction of  $\text{Fe}_2\text{O}_3$  to FeO and of  $\text{MnO}_2$  to MnO is necessary for a high efficiency of this leaching. [Sheikhshoae 2006] applied the strong chelating activities of different carbamate derivatives to remove  $\text{Ni}^{2+}$  ions from biological systems under laboratory scale.

The Fe concentrations in the three leachates with rich loaded MEA solution differ from 55 to 99 mg/l. Each ESP ash behaves specifically. Much more Fe is dissolved by the rich loaded MEA solution compared to demineralized water, even though demineralized water still has the highest part of mass in the rich loaded MEA solution. Normal reactions of  $\text{Fe}^{2+}$ , which occur in the demineralized water as oxidation and precipitation, fail to appear because complex bounded  $\text{Fe}^{2+}$  is no longer close to water molecules. To undergo the same leaching procedure for a second and even a third time [Drakonaki 1998], after having washed and dried the

residue of the first leaching experiment, could improve our understanding about the dissolution of Fe and the other elements from ESP ashes.

The results for Fe in leachates of the rich loaded MEA solution fit well to the published data of [Schallert 2013]. According to Schallert et al., Fe concentrations amounted to 48, 54, 98 and 114 mg/l for four different ESP ashes under 1:10 (g/g), 22 °C and 24 h. [Chandan 2014] published Fe concentrations in the leachates of 6.3, 6.4, 8.8 and 10 mg/l at 1:100 (g/g), 80 °C and around 150 hours for ESP ashes from hard coal-fired power stations. The longer leaching time slightly increases the concentration [Schallert 2014], the effect of higher temperature will definitely enhance the concentration, but nevertheless these concentrations confirm the results of this study when the ratio of 1:100 (g/g) is considered. A calculation of the concentrations to a ratio of 1:10 (g/g) corresponds to an increase by a factor of ten.

Because of glass leaching further analytical work on this subject should also include the determination of dissolved silicon and, when the pH of the leachate with demineralized water after 24 hours is below 10, then as well of ammonia.  $\text{NH}_3$ , which derives from high dust SCR Denox plants as a small slip, condensates as ammonium hydrogen sulfate ( $\text{NH}_4\text{HSO}_4$ ) when the flue gas temperature drops significantly during the passage of the flue gas air preheater and a surplus of sulfuric acid is available. To a high extent this condensation occurs on the surface of fly ash particles.  $\text{NH}_4\text{HSO}_4$  reacts acidic as sulfuric acid and neutralizes the free lime when fly ash particles are leached with water.

If the glass surface is partly opened by leaching, then there is an additional access to the inner surface and to the crystalline material inside. This might affect the time dependent leaching behaviour.

When dissolved species in water are balanced e.g. for river water, then the difference of the sum of cations to the sum of anions is the alkalinity of carbonate and of hydrogencarbonate if not determined. This is also correct when demineralized water is used for leaching. [Matusiewicz 1980] confirmed the release of carbonate from ESP ash by leaching with demineralized water by ion chromatographical analysis. Approx. 1.5 meq/l  $\text{CO}_2$  [Sigg 2011] is likely to be collected from the air on top of a water solution. During the leaching process the suspension is moved from time to time thus scrubbing of  $\text{CO}_2$  from the air inside the closed bottle will occur. The other part is released from the carbonates of the ESP ashes ( $\text{CaCO}_3$  and  $\text{MgCO}_3$ ). [Elsewi 1980] measured 2.2 meq/l for the sum of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  at a solid to liquid ratio of 1:10, over 24 h and at room temperature for a US western coal ESP ash. This scrubbing

effect during the leaching experiments and the dissolution from carbonates of the ESP ashes will also occur for the rich loaded MEA solution.

Small amounts, which are missing in the ion balance, are definitely related to a few anions such as borate, silicate and molybdate which are not analysed in the present study. At 1:10 (g/g) there should be a small contribution of these anions to the ion balance, but at ratios of 1:1000 these compounds can be probably neglected.

A small part of the gap in the ion balances for the rich loaded MEA solution is related to carbamate ions. These carbamate ions at least stabilize  $\text{Fe}^{2+}$  concentrations in the leachate. Carbamate ion acts as a ligand and likely forms quite stable complexes. Further research should address their impact.

Complexing agents have been used for the leaching of fly ashes from waste incineration plants, but only once from a lignite coal-fired power plant to extract heavy metals [Janos 2002]. After ball milling of this fly ash sample, Janos applied a ratio of 1:10 at room temperature, taking liquid samples several times during the 24 hour extraction time. He used 0.1 mol/l EDTA- $\text{Na}_2$  solution in deionized water as a liquid. EDTA- $\text{Na}_2$  is ethylenediaminetetraacetic acid, to the half neutralized by sodium hydroxide to form a salt. This 0.1 mol/l solution has a pH of 7.5, which encourages as well the dissolution of heavy metals. The lignite fly ash possesses a Fe concentration of 2.97 % and the Fe concentration in the leachate was approx. 95 mg/l after 24 hours, with further increases after that time. As a result of model calculations Janos estimated an equilibrium value of 158 mg/l, suggesting that approx. 5 % of Fe can be dissolved from this lignite ESP ash by a strong chelating acid with a concentration of 0.1 mol/l. When compared with the carbamate ions for complexation, it has to be considered that each EDTA- $\text{Na}_2$  molecule has two ligands for stabilizing the  $\text{Fe}^{2+}$  in the solution and the carbamate concentration in the rich loaded MEA solution was approx. 1.9 mol/kg, calculated from the molar concentration of the rich loaded MEA solution and the loading without any consideration of the small amounts of hydrogencarbonate/carbonate. Therefore, the strength for complexing  $\text{Fe}^{2+}$  ions by MEA carbamate ions is much lower when compared to the strength of EDTA- $\text{Na}_2$  ions for complexation in demineralized water.

### 5.3 Effect of the MEA concentration

Because the amount of ESP ash was constant for these tests, the results for Fe clearly indicate that there is a strong complex of MEA carbamate to Fe, most likely  $\text{Fe}^{2+}$ . This dependency must be taken into account when improvements are discussed that are based on a higher molarity of MEA. It is recommendable to repeat this examination with several MEA concentrations, e.g. 0.5, 1.0, 3.0, 5.0, 6.0 and 7.0 M, rich and lean loaded, 1:10 (g/g), 22 °C, 24 h, in order to investigate how it will affect the process.

The behaviour of the ESP ash PP4 is remarkable when the missing alkalinity of ion balance is considered (Table 5). For the ESP ashes of PP3 and PP6 the missing alkalinity, which is the sum of carbonate and hydrogencarbonate, is two to four times higher for the highest molarity of MEA tested. Most likely, this is an effect of the ESP ash composition. Only the ESP ash PP4 possesses a pH value of 9.5 at 1:10 (g/g), 22 °C and 24 h for demineralized water (Table 2), which predominantly derives from the ratio of Ca to S in the leachate. If the free CaO content is sufficiently available, which is normal for CaO contents above 2 % [Kautz 1986], then the pH values in the leachates of ESP ashes will be typically between 10.4 and 12.5 [Moreno 2005], who used a solid to liquid ratio of 1:10 (g/g), room temperature, 24 hours and demineralized water. But if the ratio of Ca to S in the leachate is below 1.38 (meq/meq), then the pH predominantly drops to values below 10 [Moreno 2005]. This is related to the strongly acidic sulfur compounds at the surface area of the ESP ash particles. Sulfur is added to the surface area of the fly ash particles by condensation of  $\text{NH}_4\text{HSO}_4$ , which takes place in the air preheater when the flue gas temperature drops to 120-140 °C. Secondly, sulfuric acid itself can directly condensate at the surface of fly ash particulate matter at the cold end of the air preheater. Both, sulfuric acid and ammonium hydrogensulfate, are liquids when their condensation occurs. Both react strongly acidic and, if in contact to carbonates,  $\text{CO}_2$  will be released to the flue gas and sulfates are formed. It is assumed that sulfuric acid and/or ammonium hydrogensulfate concentrations on the surface of ESP ash particles cause the decrease of the pH in the leachate of the ESP ash PP4 as well as the lowered alkalinity values. Additional leaching tests with less “alkaline” ESP ashes would help confirm these findings and control the ion balances.

## 5.4 Influence of added degradation products

Carbonic acid concentrations result from oxidative reactions of the MEA solution and form heat stable salts (HSS). These reactions start when the lean solution enters the absorber and stop at the inlet to the stripper column when the rich solution loses CO<sub>2</sub> and O<sub>2</sub> by degassing. The accumulation cannot be avoided because the HSS are not destroyed thermally at the stripper temperature, thus the impact of these degradation products on the leaching of fly ash particulate matter must be considered. Formate is mainly produced, but does not have any effect on the dissolution of Fe [Schallert 2013]. Acetate behaves non-uniformly in this study, thus more data are necessary for a better understanding. A glycolate concentration of 50 mmol/l slightly raises the amount of Fe dissolved from fly ash particulate matter, but it takes many operational hours to reach such a concentration level of glycolate as tested. Most likely, the effect of glycolate can be neglected because of this slow rate of formation in the rich solution and the slight impact at the high concentration as examined. 50 mmol/l oxalate does not necessarily increase the dissolution of Fe, but limits the concentration of Ca by precipitation, maybe as well for Fe. This result confirms former investigations of one ESP ash [Schallert 2013].

Examinations by [Schallert 2014] with two degraded lean 5 m MEA solutions, which were treated by ion exchange to reduce the Fe concentration before using this liquid for leaching, document that also other degradation products such as HEGly (N-(2-hydroxyethyl) glycine) or HEF (N-(2-hydroxyethyl) formamide) do not impact the dissolution of Fe significantly.

When HEGly, HEF and other degradation products are available as commercial chemicals with certificates, then it is valuable to conduct similar leaching tests in order to identify their direct impact.

## 5.5 Relevance of the solid to liquid ratio

At a ratio of 1:10 (100 g/kg), the bandwidth for the Fe concentrations in the leachates of the three ESP ashes is 55 mg/l (PP4) to 99 mg/l (PP3). The ratio of PP3 to PP4 amounts to 1.8. At 1:200 (5 g/kg) this ratio drops to 1.3 and at solid to liquid ratios of 1:10000 (100 mg/kg) it will be even closer to 1. The composition of the ESP ash influences the concentrations in the

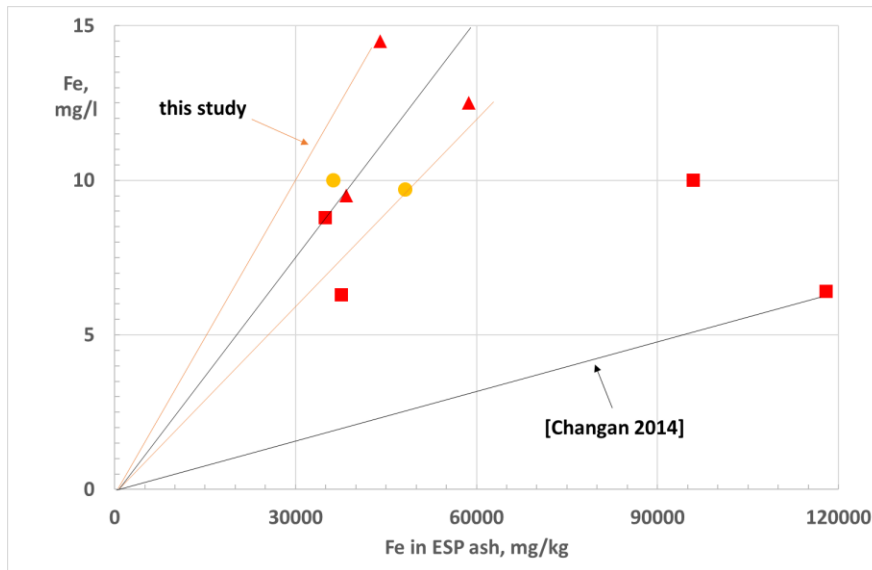
leachate stronger at 1:10 compared to 1:100, but at 1:200 all ESP ashes react quite similar for Fe.

The Fe results published by [Schallert 2014], which were based on a treated, lean 5 M MEA solution, lead to linear regression curves. The Fe concentration levels of this study are lower at the ratio 1:10 (100 g/kg). Possible reasons could be the effect of the enriched degradation products, which are accumulated in the real lean 5 M MEA solution from the pilot plants and/or simply the difference in the leaching behaviour for the rich and lean loaded MEA solutions. The regression curves of the other heavy metals also deviate from the former published ones likely by the same reason(s).

A comparison to the published data of [Chandan 2014] is only possible for Fe (Table 16, Figure 57). The results of Chandan are mainly lower than those of this study for rich solution in spite of longer leaching time and higher temperature for leaching. If the results of this study for the lean 5 M MEA solution are additionally considered (tables 12 and 13), then there is an overlapping of bandwidths for the dependency of Fe in the leachate on the Fe concentration in the ESP ash and a confirmation of the results of this study.

**Table 16:** Comparison of leachate results for Fe at a ratio of 1:100 (g/g)/22 °C/24 h to the results of [Chandan 2014] (80 °C, around 150 h), and their relating Fe content of the ESP ashes

		[Chandan 2014]								
		PP3, 2012	PP4, 2012	PP6, 2012	PP3, 2015	PP7, 2015	Ghent	Kentucky	China bit.	Bulgaria sub.
		rich 4.3 M MEA	rich 4.3 M MEA	rich 4.3 M MEA	lean 5 M MEA	lean 5 M MEA	rich 5 M MEA	rich 5 M MEA	rich 5 M MEA	rich 5 M MEA
		1+100	1+100	1+100	1+100	1+100	1+100	1+100	1+100	1+100
		estimated	estimated	estimated						
	<b>g ESP ash/kg</b>	10	10	10	10	10	10	10	10	10
<b>Fe in ESP ash</b>	ppm	44062	38467	58750	36369	48259	37590	117950	34930	95970
<b>Fe in leachate</b>	mg/l	14.5	9.5	12.5	10.0	9.7	6.3	6.4	8.8	10



**Figure 57:** Bandwidth of the results regarding this study ((triangles PP3, PP4 and PP6, 2012) and circles (PP3 and PP7, 2015)) compared to published data (squares [Changan 2014]), red colour for rich, ochrous for lean 5 M MEA

For all studied elements and compounds three element or compound specific characteristics are observed:

1. A linear decrease by changing the ESP ash concentration from 100 to 5 g/kg,
2. stable concentrations independent of the ESP ash concentration, and
3. a power function decrease from high ESP ash concentration to low.

Salts show a linear decrease when their solubility in water is much higher than observed in the leachates and the Gibbs free energy decreases by dissolution. Sodium and potassium sulfates are easily dissolved in a linear dependency on the ESP ash mass to be leached. Na and K ions are stabilized in water as ion to water complexes. In the rich 5 M MEA solution it is probably correct as well. Sulfate as a common ion will influence the dissolution of anhydrite ( $\text{CaSO}_4$ ).

Stable concentrations in the leachate occur because solubility equilibria are reached during the leaching process. The concentrations of Ca and Al point out this characteristic. The differences in the concentration level for the ESP ashes are related to the ESP ash specific composition of the leachate. Most likely, hydrogenphosphate ( $\text{HPO}_4^{2-}$ ) forces the precipitation of calcium hydrogenphosphate and aluminium phosphate. When the solid to liquid ratio is changed to around 1:1000 (g/g), then these concentrations in the leachate are so small that the solubility is no longer limited. Laboratory tests with leachates of ESP ashes, to which small



amounts of lime ( $\text{Ca}(\text{OH})_2$ ) are added, are recommended to confirm the behaviour of hydrogenphosphate.

The power function decrease to lower ash concentrations can be interpreted as an approach to the solubility limits at high ash concentrations. Most likely, it is as well hydrogenphosphate that withholds the concentration level of Fe. More solid to liquid ratios near to 1:10 (100 g/kg), maybe 1:20 (50 g/kg), 1:5 (200 g/kg) and 1:2 (500 g/kg) should be studied to clarify these relationships.

The results of the ion balance (Table 11) indicate that the gap of alkalinity (sum of carbonate and hydrogencarbonate) increases to higher ESP ash concentrations for the ESP ash of PP3 and of PP6, but not for PP4. It is assumed that the ESP ash of PP4 has lost carbonated free CaO by the reaction with sulfuric acid or with ammonium hydrogen sulfate after this condensation has happened along the flue gas pathway. That is likely why there is no increase of the gap of alkalinity for PP4 when the ESP ash concentration increases. The slopes for PP3 and PP6 are different because the compositions of these ESP ashes still differ from each other. It is assumed that low amounts of  $\text{CaCO}_3$ , most likely below 1%, are still available during the leaching experiments. [Querol 2000] examined ESP ashes for the calcite ( $\text{CaCO}_3$ ) concentration by x-ray diffraction technique. For each ESP ash from hard coal-fired power plant Querol published the value zero, but no limit of detection was mentioned. Because this technique is not very sensitive to low concentrations, ESP ashes might possess several tenths % of  $\text{CaCO}_3$ , which could be dissolved and could close the ion balances. Further work on this subject including borate, silicate and molybdate is recommended.

The observed tendency (Figures 44-46) that at ratio of 1:200 (g/g) relatively more Fe is dissolved from the ESP ash compared to a ratio of 1:10 (g/g) should be confirmed in additional experiments. The results might indicate that there are systematic errors. One error could result from the impact of the weighing; another error might occur because fly ash particles with diameters smaller than  $0.45 \mu\text{m}$  pass the membrane filter and contribute to the analytical result. Future investigations should include the same conditions as in this study, but additionally a variation in the absolute mass of the ESP ash by a factor at least of two and two different membrane qualities of  $0.45 \mu\text{m}$  and  $0.2 \mu\text{m}$  for filtration.

Future work should focus on solid to liquid ratios near to 1:1000 (g/g) to generate data for the prediction of the Fe concentrations in the first hundred hours of the CC plant operation. A set

of ratios like 1:10, 1:500, 1:1000 and 1:5000 (g/g) is a good basis for the extrapolation to smaller ESP ash concentration in the lean 5 M MEA solution.

## 5.6 Results of repeatability measurements

Two ESP ashes that significantly differ in their composition are used for the repeatability measurements. These differences are also identified in the compositions of the leachates, e.g. Na, Mg, P and S. The concentrations of the heavy metals do not differ significantly in the leachates except of Mn. There is no main difference according to the results of the repeatability measurements when the results of both ESP ashes are compared. Only at very low concentrations, near to the LOD, the variation coefficient increases significantly. For the elements Na, K and partially P the analytics and/or the sampling of the ESP ash for analytics must be studied for improvements.

In spite of these positive results it should be taken into account that 5 M MEA solutions distinguishes notably from acidic water solutions for which lower limits of detection can be achieved. It is recommended to participate in a round robin test in order to prove sufficient accuracy.

The results of Fe, achieved at 1:100 (g/g)/22 °C/24 h (tab. 12 and 13), fit to those of [Chandan 2014] in spite of a longer leaching time and a higher temperature (Figure 57).

## 5.7 Prognosis of fly ash and dissolved Fe accumulation

The results of the prognosis based on the leachate composition at 1:1000 (g/g) of the ESP ash PP7 (Table 13) underline that only Fe is dissolved from ESP ash at ratios of 1:100000 (10 mg/kg) or smaller. All the other studied heavy metals will not be detected because of their extremely low concentration at these ratios.

This prognosis does not take into account effects by

- the absorber temperature, which is site specific, but higher than the room temperature,

- the impact of formed degradation products, which enhance the Fe dissolution, especially when high concentrations of these degradation products are formed, and
- longer leaching times (> 24 h), which might open the cenosphere of the fly ash particles and therefore might increase the concentrations of the heavy metals of concern.

But this prognosis at least points out which concentrations of Fe and of the other heavy metals can be expected. The used leachate data of ESP ash PP7 are neither a best case nor a worst case, but these data are the best available data for an estimation of the Fe concentration shortly after the beginning of CC operation.

It is not yet known if fly dust behind the FGD will behave similarly to the studied ESP ashes of the hard coal-fired power stations. While there are data available regarding the composition of fly dust, data regarding the leachate composition of the fly dust are still missing. Therefore, it is explicitly recommended to perform isokinetic sampling of the particulate matter at the outlet of the FGD, when the hard coal-fired power plant is operating under full load, and to collect at least 2.5 mg of dried fly dust per sample on a quartz filter. This sampling should be realized six times, then two of these six filters can be leached by 50 g of lean 5 M MEA which would be a ratio of 1:20000 (50 mg/kg). Fe can still be determined in this leachate, when a LOD value of 0.02 mg/l is applied. The next two filters can be analysed for all parameters of the ESP ash with the exception of Si. This procedure allows for calculations on the amount and composition of fly ash, including the relative importance of the dried droplets from the FGD. The last two filters can be used for microscopic views on the collected fly ash particulate matter by scanning electron microscope (SEM) technique. Additionally, ESP ash from this PP, sampled parallel to the isokinetic fly dust measurements, should be leached at four solid to liquid ratios (1:10, 1:1000, 1:10000 and 1:20000 (g/g)) for comparison. This procedure is suitable to gain the information about the fly dust concentration entering the CC plant, the variation of the fly dust concentration within a well-known time period, the composition of the fly dust and their leachability. Additional measurements when the power plant is firing another coal mixture, at part load of the power plant and at a changed liquid flow inside the FGD (still at full load of the power plant) are highly advised. The results of these measurements should be available before any planning of a CC plant starts.

[Chandan 2014] studied the impact of fly ash on the formation of degradation products at a solid to liquid ratio of 1:100 (g/g) by using different ESP ashes. The results indicate that 6 to 10 mg/l Fe are sufficient to catalyse the formation of degradation products. The conclusion is

to keep the fly ash concentration in the liquid significantly below 10 g/l. [da Silva 2012] ran a test with an ESP ash at approx. 1:300 (g/g) over 501 hours and at 55 °C. Da Silva et al. documented a slight increase of degradation products due to the added ESP ash, assuming that the dissolved Fe caused this increase. As a result, the level of 3,4 g fly ash per kg is still too high because the formation of degradation products was still catalysed.

Both publications focused mainly on the formation of degradation products, not on the dissolution of heavy metals from the fly ash or the emission of NH<sub>3</sub>. Chandan's results of dissolved Fe at 1:100 (g/g) are similar to the results of this study for the ESP ashes of PP3 and PP7, both leached at 1:100. There are some differences due to the leaching time, the temperature and the liquid for leaching (Chandan used a rich 5 M MEA in contrast to a lean 5 M MEA in this study). Possibly, the conditions in the Chandan study may have favoured the dissolution of Fe but were compensated by ESP ashes with a lower tendency to release Fe.

A close look at Table 13 for the average values of the heavy metals at 1:100 (g/g) reveals that there is a great surplus of Fe by mass compared to the other heavy metals. Based on molecular weights the concentrations are for Fe is 173 µmol/l (µM), for V 5.9 µM, for Cr 4.2 µM, for Mn 4.0 µM, for Ni 0.5 µM and for Cu 2.7 µM. The ratio of Fe to the other heavy metals slightly changes due to the differences of the molecular weights. To evaluate this spectrum of heavy metals, the element specific effect as a catalyst and as well in combination or as a mixture should be known.

[Goff 2005] performed O<sub>2</sub> mass transfer experiments with an agitated reactor, FTIR gas phase emission measurements and MEA solutions to which Fe<sup>2+</sup> sulfate or Cu<sup>2+</sup> sulfate could be added in aqueous solution. The fresh lean 5 M MEA solution has been contaminated by the production of MEA to a rather small concentration of 0.2 µM Fe (11.2 µg/l Fe), not analyzed in this solution, but calculated from the detected concentration of Fe in the delivered 99.9 % MEA. When Goff's results concerning the addition of Fe to the lean 5 M MEA solution inside the agitated reactor are transferred to a CC plant, which has just started continuous operation with cleaned flue gas of a hard coal-fired power plant, then the following conclusions can be drawn:

- In spite of a 5 M MEA solution without any contamination and no corrosion of the installed materials inside the CC plant at all, Fe will be leached immediately from the absorbed fly ash particulate matter. After approx. 12 hours of operation the Fe concentration will reach around 0.2 µM Fe, when 1 mg/m<sup>3</sup> fly ash is absorbed and a

specific enrichment factor of  $0.8 \text{ m}^3 / l_{\text{inv}} * h$  is applied. The time dependent increase of the Fe concentration, especially at those very low concentrations of Fe, will favour the catalytical oxidation of MEA and increase the emission of  $\text{NH}_3$ .

- After the Fe concentration has climbed up to around 0.036 mM Fe (approx. 2.0 mg/l Fe), the emission level of  $\text{NH}_3$  will only slightly be impacted by the further increase of the Fe concentration in the solution. Approx. 2000 hours are needed regarding the above mentioned conditions of the CC plant.

The absolute concentration of  $\text{NH}_3$ , which is emitted from the CC plant at the beginning of the CC operation and which increases over time, also depends on various factors, including e.g. the  $\text{O}_2$  concentration of the flue gas, the  $\text{CO}_2$  capture rate, and the temperatures of the solution within the absorber column. Additionally, there will be an impact of other heavy metals, which are leached from the absorbed fly ash particulate matter, on the  $\text{NH}_3$  emission level.

[da Silva 2012] demonstrated that 3.4 g ESP ash per kg rich solution already initializes additional degradation by catalytic enhancement. Therefore, the limit for accumulated fly ash particulate matter is proposed to be less than 1 g/kg which could result in a Fe concentration of 1.4 mg/l (25  $\mu\text{M}$ ) for the lean 5 M MEA solution.

Consequently, the calculations to reach the accumulated fly ash concentration of 1 g/kg (Table 15) reveals a quite short operating time of 1.333 hours, based on  $1 \text{ mg}/\text{m}^3$  absorbed fly ash and a sEF of  $0.8 \text{ m}^3 / (l_{\text{inv}} * h)$ . To design greater sump volumes for lower enrichment factors will increase the capital costs and the operational costs for the exchange of the liquid inventory and for disposal. Because the fly dust emission of the new coal-fired power plants at that time of measurements can be below  $1 \text{ mg}/\text{m}^3$  [Gutberlet 1984], [Fahlke 1994] and [Meij 1994], the fly dust concentrations at the emission point should be intensively studied by manual, isokinetic measurements to get reliable fly dust data. Secondly, the design of the prescrubber or the direct contact cooler should be optimized to reach fly dust concentrations upstream the CC absorber equal or less than  $0.6 \text{ mg}/\text{m}^3$  ( $0.3 \text{ mg}/\text{m}^3$  fly ash assumed). This level of fly ash or fly dust is essential for the operation of the liquid inventory at least for 4000 hours at full load before a fly ash concentration of 1 g/kg is reached in the lean 5 M MEA solution based on  $0.3 \text{ mg}/\text{m}^3$  fly ash.

When fly dust is scrubbed out by the rinsing lean solution in the absorber column, the leaching of Fe and of all other elements will start and will not stop by the deposition of the particulate

matter or by e.g. capturing in cartridge filters. Due to the leaching of glass longer terms of leaching, maybe up to 1.500 h, should be studied.

## 6 Summary, conclusions and recommendations

### 6.1 Summary

Flue gas from coal-fired power plants still contains small amounts of fly dust. This fly dust consists of fly ash particulate matter passing the desulfurization plant and of small, dried droplets from this cleaning device. This flue gas quality is used for CC plants with flue gas of coal-fired power plants. The CC technology, which is the most developed technology, uses a mixture of alkanol amine(s) in water in a closed cycle to scrub out CO<sub>2</sub>. Particulate matter, which is absorbed in the absorber column of the CC process, accumulates over time. The extent of accumulation depends on the absorbed mass flow relative to the dust, the liquid inventory and the time. Some accumulation is unavoidable during operation.

Particulate matter can partly dissolve in liquids depending on the solubility of the compounds belonging to the particulate matter, liquid properties, concentration, time and temperature. Much research has been devoted to the solubility of these solids in water, but little is known regarding the solubility in alkanol amines, even in the most intensively studied MEA.

Fly dust behind FGD as a representative sample needs costly, isokinetic sampling over several hours to collect some mg as an absolute mass. Running comparable tests and fulfilling additional analytical work requires around 20-50 g. ESP ash from different hard coal-fired power stations is an acceptable proximate instead of fly ash (before FGD) or fly dust (behind FGD) because it is easily accessible and because Fe is mainly independent of the particle size distribution of fly ash [Meij 1994].

The main part of this study focuses on parallel tests using one rich loaded 5 M MEA solution for the leaching of three different ESP ashes under various conditions. Firstly, the results of leaching over 24 hours, at room temperature and at a solid to liquid ratio of 1:10 (g/g) are compared for three liquids, the rich loaded 5 M MEA, the non-loaded 5 M MEA and demineralized water. Secondly, the molar concentration of the rich loaded 5 M MEA solution is thinned by demineralized water to get another two molar concentrations and then each solution is applied for leaching at 1:10 (g/g). Thirdly, 50 mmol/l of three carbonic acids (acetic, glycolic and oxalic acid) are added to three samples of the rich loaded 5 M MEA solution and

then each liquid is used for leaching. Fourthly, the solid to liquid ratio is varied from 1:10, 1:50 to 1:200 (g/g). The remaining study describes investigations on the repeatability of the whole procedure. Leaching, filtration and analyses are performed four times for each ESP sample at solid to liquid ratios of 1:100, 1:1000 and 1:10000 (g/g). These analytical results are used to forecast the Fe and as well as the other heavy metal concentrations for the early beginning of a CC plant operation considering technical conditions and distinct absorption of fly ash particulate matter.

The main results are summarized as follows:

- The rich loaded 5 M MEA solution dissolves an enormous amount of Fe compared to pure water. Each ESP ash dissolves Fe and the other heavy metals specifically. At a solid to liquid ratio of 1:10 (g/g), the ESP ashes dissolve 55 mg/l to 99 mg/l Fe.
- The Fe concentration increases disproportionately with increasing molar concentration of the rich loaded MEA solution. This indicates that Fe is probably stabilized by the carbamate concentration, most likely by complexation. A similar behaviour is likely for Mn. For V, Cr and Cu the increase of their concentrations is lower than the increment of the molarity. The Ni concentrations are too low for any evaluation.
- The glycolate concentration as a degradation product enhances predominantly the dissolution of Fe at the high concentration of 50 mmol/l. The oxalate concentration may suppress the Fe concentration by precipitation, but not necessarily. The oxalate concentration in the leachate reduces the Ca concentrations significantly by precipitation and raises the phosphate concentrations.
- With a lower solid to liquid ratio the concentration of all analysed elements and compounds decreases, but specifically for each element/compound and ESP ash when solid concentrations of several g/l occur.
- Each ESP ash has its own specific pattern for the dissolved heavy metals at a solid to liquid ratio e.g. 1:10 (100 g/kg). For ratios < 1:1000 (< 1g/kg) the dissolved concentrations for different ESP ashes become quite similar and the specific character of each ESP ash becomes less important.
- The repeatability values point out variation coefficients predominantly below 5 % for Mg, Ca, S, Fe, V, Cr and Mn.



- The leachate results at 1:1000 (g/g) for the ESP ash PP7 are the best available data for further extrapolation, because all heavy metals except of Ni could be detected compared to the ESP ash PP3.
- Apart from main elements such as Ca, Mg and S, only Fe is forecasted to be detected in the lean 5 M MEA solution of a CC plant after 24 h of operation, when 1 mg/m<sup>3</sup> of fly ash is absorbed by the circulating liquid and an enrichment factor of 0.8 m<sup>3</sup>/(I<sub>inv</sub>\*h) is applied.
- A linear increase of the Fe concentration, starting with a few µg/l within 24 h of operation and significantly later accompanied with low concentrations of V, Cr, Cu and Mn in µg/l, derives from the leaching of absorbed fly ash particulate matter. It is assumed for the calculations that fly dust consists of fly ash completely.
- Glass leaching occurs as well.

To improve the performance of a CC plant the inlet fly dust concentrations (50 % fly ash assumed) are recommended to be lower than 0.6 mg/m<sup>3</sup> (STP, dry, 6 % O<sub>2</sub>) to control the accumulated fly ash below 1 g/kg for at least 4000 hours, when an enrichment factor of 0.8 m<sup>3</sup>/(I<sub>inv</sub>\*h) is applied. If the dried droplet part of the fly dust also releases Fe strongly to the leachates, then this will shorten the time period with low impact of degradation products (less than 4000 hours).

These results underline the relevance of leaching to CC plants and strive for a better understanding of the solubility of various elements and heavy metals, especially Fe, in MEA solutions and of relevant leaching parameters.

## 6.2 Conclusions

Fe<sup>2+</sup> is supposed to be intensively complex bounded in the rich loaded MEA solution.

For example, at 7 M MEA, which could save investment costs, an even stronger leaching of Fe from the accumulated fly ash will occur compared to the maximum molarity used in this study. This directly affects the emission and degradation of the MEA solution and must be considered economically because of a reduced life time of the liquid inventory.

In order to compensate the losses of MEA by emission, degradation and reclaiming, the dosage of fresh MEA for the CC plant should be applied continuously by pumps. This is important to avoid significant variations of the liquid composition due to changing molarities. There is no indication available that the leaching of accumulated fly ash causes an exponential increase of the Fe concentration over time. This can be concluded because the results of the Fe concentrations, that are leached from ESP ashes at different solid to liquid ratios, do not increase exponentially to high ash concentrations, but by a power function with exponents between 0.69 and 0.84. To low ash concentrations (< 1g/kg) the decrease will be linearly towards extremely low ash concentrations shortly after the start-up of the CC plant. When similar concentrations of Fe, Cr and Ni occur in the lean 5 M MEA solution, then the leaching of absorbed fly ash cannot be the main source, especially when Ni is observed in the early beginning of the CC plant operation. Most likely, it is related to the corrosion of stainless steel material.

### **6.3 Recommendations**

For the planning of a demonstration or commercial CC plant it is advisable to distinguish between imported coals and local ones. Imported coals are predominantly low ash coals because the transport costs have to be considered. These coals will be burnt as coal mixtures that will minimize the differences for the ESP ashes or the fly ash behind the cleaning devices when samples are taken during longer operation time. Local coals might be cheaper due to the low transport costs and the firing system can be more closely adapted to optimal conditions. But the coal ash concentration might be higher, the ESP ash composition and the leaching behaviour might be quite different compared to ESP ashes based on imported coals. In any case, ESP ashes, fly ash and fly dust samples should be analysed for the main elements, the spectrum of heavy metals and for additional parameters as ammonia and free CaO (only ESP ash).

More pre-studies should be carried out for retrofits of CC plants compared to new CC plants behind new hard coal-fired power plants. The composition of the ESP ash and the fly dust concentration behind the last cleaning device should be sampled several times (at full load, at

half load, and when different coals are burnt) to recognize variations and to consider their impact on the performance of the CC operation.

When a retrofit of a CC plant behind a coal-fired power plant is planned, then an excellent knowledge about the flue gas composition is one important precondition for successful implementation. This means that beside to the gaseous concentrations, the particle size distribution including aerosols, the particle mass and their composition must be known for full and part load, for different coals to be burnt and for non-stationary conditions.

In addition to that, it is very recommendable to perform manual, isokinetic dust measurements at the outlet of the FGD in order to identify if there is any difference between the leaching of ESP ash and the leaching of fly dust, mainly focussing on the concentrations of Fe and the other heavy metals concerned. The procedure should at least generate a set of 6 samples with a dried, minimum mass of approx. 2.5 mg each. Two filters are used for scanning electron microscope (SEM) analysis, two for the determination of the absolute element concentration by ICP, and two for leaching with 50 g lean 5 M MEA with leachate analysis afterwards. Additionally, two blank samples (quartz filter) should be analysed by ICP and two blank filters are used for the complete procedure of leaching.

The composition of the ESP ash and the fly dust concentration behind the last cleaning device should be sampled several times (at full load, at half load, and when different coals are burnt) to recognize variations and to consider their impact on the performance of the CC operation. If a gas-gas-heater (GGH) is applied for reheating the flue gas flow behind the FGD, then the state and the impact of the GGH on the fly dust quality should also be considered.

Because the glass matrix of the fly ash particles undergoes leaching, it is worthwhile to study how the composition of the leachate will change during long-term experiments. At least two ESP ashes should be tested at a solid to liquid ratio of 1:10 (g/g), room temperature and over 24 hours and longer times, using a lean loaded 5 M MEA solution. Additionally, silicon should also be analysed.

Leaching experiments with several molar concentrations of MEA up to 7.0 M, rich and lean loaded, are recommended to confirm the higher leaching effect for Fe. Then a higher molarity of the MEA solution e.g. 7 M can be evaluated economically.

A similar study design should be applied for alternative solvents to identify which effect ESP ashes have on the concentrations of Fe and the other heavy metals with respect to defined leaching conditions.

When HEGly, HEF and other degradation products are available as commercial chemicals with certificates, then it is valuable to perform similar leaching tests in order to identify their direct impact.

The list for the elements to be analysed from ESP leachates should be generally completed by silicon, boron and molybdenum. If the pH of the leachate is below 9.5 for a solid to liquid ratio of 1:10 (g/g), 22 °C and 24 h, when demineralized water is used for leaching, then the ammonia concentration of the fly ash sample should also be determined.

Future work should focus on solid to liquid ratios near to 1:1000 (g/g) to generate more data for the prediction of the Fe concentrations in the first hundred hours of the CC plant operation. A set of ratios like 1:10, 1:500, 1:1000 and 1:5000 (g/g) is recommended for the extrapolation to smaller ESP ash concentrations.

Leaching ESP ashes two or three times [Drakonaki 1998] with a short washing in between and drying afterwards will provide additional information on how much of Fe and of the other elements and compounds can be dissolved.

Participation in a round robin test for leachates of at least two different ESP ashes leached at three solid to liquid ratios would ensure sufficient accuracy. Future investigations should focus on laboratory tests, similar to [Goff 2005], but using lean 5 M MEA leachates of ashes over 24 hours and at room temperature instead of fresh MEA solutions dotted with different heavy metal concentrations. It is proposed to examine three different fly ashes and four different solid to liquid ratios to gain experimental data of the impact of heavy metal combinations on the formation of NH<sub>3</sub>.

To achieve a fly dust concentration of 0.6 mg/m<sup>3</sup> (STP, dry, 6 % O<sub>2</sub>) or 0.3 mg/m<sup>3</sup> fly ash is a challenge, but beneficial for a good performance of the CC plant according to the emission of NH<sub>3</sub> and the accumulation of Fe and of the other heavy metals leached from absorbed fly dust. Therefore, the direct contact cooler or the prescrubber (Figure 1) in front of the CC absorber should be optimized for an enhanced removal of fly dust.

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