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SHORT COMMUNICATION

Investigation of the contamination of a fly ash sample during sample preparation by air classification

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Abstract Information on the size dependence of the concentration of pollutants in fine-grained residues is required for the design of classification processes for their processing. For such an analysis, the samples have to be classified prior to chemical analysis. Depending on the particle size range of the residue, a classification method has to be selected. For very fine material, air classification is a suitable method. In this work, the results of the classification of fly ash from a biomass combustion plant with an air classifier are discussed with respect to the observed sample contamination. The chemical analysis of the produced size classes for heavy metals yielded unexpected results. For most heavy metals, the mass balance resulted in a recovery rate of about 100 %; however, for Cr and Ni, the recovery rate was way above 100 %. A more detailed analysis of the data revealed that the ratio of the excess of Cr to Ni in the fly ash was nearly the same as the ratio of Cr to Ni in the material of parts of the classifier. Therefore, erosion of some material from the classifier can be assumed to have caused the contamination of the sample. For the classification of samples, which have to be analysed for Cr and Ni, a classifier has to be used which is made of a material other than stainless steel.

Keywords Dust sample · Sample preparation · Classification · Heavy metal contamination

Introduction

The dust collected from the off-gas of industrial processes is a fine-grained material with a particle size distribution that can range from submicron particles to particles with a diameter of several hundred micrometres. The chemical analysis of the dust depends very much on the type of process where it originates from. From an economic point of few, recycling or reuse of the collected dust is attractive because dumping of these residues is usually very costly. Direct recycling or reuse is often not possible because some unwanted components exceed their concentration limits. In that case, pre-treatment processes for the dust are required. In dust, which originates from high temperature processes, the composition of coarse and fine particles can be quite different. In particular, for the volatile components, which were gaseous during the process and condense when the off-gas cools down, the concentration in the fine particle fraction is usually much higher (Dahl et al. 2009; Fedje et al. 2010; Ma 2008). One example for such a dust is the fly ash from biomass combustion. This fly ash can be utilized as a soil conditioner in forests provided that the limits for the heavy metal concentrations are not exceeded (Haglund 2008; Steenari and Lindqvist 1997). However, depending on the kind of biomass used for the combustion, the concentrations of some heavy metals, especially Cd, Pb, Zn and As are often above the legal limit. For the decision if classification can be used to split such fly ash into two fractions, where the heavy metals are enriched in the fine fraction and depleted in the coarse fraction, the size dependence of the concentration of these components is required. In Table 1, the measured concentrations of several heavy metals are shown for a fly ash sample collected from the fabric

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Table 1 Heavy metal concentrations in the different particle classes of fly ash from a biomass combustion plant (Lacher 2007)

Fly ash particle class	Fly ash	F1	F2	F3	F4	F5	F6
Total mass fraction	1.0	0.116	0.161	0.154	0.202	0.192	0.175
Mass median diameter in µm	12	3.3	4.0	9.8	17	27	50
Heavy metals in mg/kg (d.w.)							
As	19.4	56.2	34.9	22.1	14.2	9.8	9.7
Cd	29.9	53.4	52.5	38.0	29.6	17.5	6.1
Co	16.1	11.9	20.1	18.7	17.0	17.3	20.2
Cr	64.6	233.6	637	548	188	118	138
Cu	176	345	275	211	151	109	75.7
Ni	59,6	107	406	335	138	105	123
Pb	161	462	220	147	114	83.1	38.6
Zn	3,680	14,200	4,980	3,270	2,170	1,250	731

filter of a grate-fired biomass combustion using wood chips as fuel (Lacher 2007). The sample was split into particle classes with different particle sizes using an air classifier. This was done in a way that in the first classification run, the finest particles were separated from the fly ash as Particle Class 1. The coarse particles were used as feed for the next classification run, where under a reduced speed of the classifier the coarser particles were separated as Particle Class 2. This procedure was repeated until the fly ash was split into six particle classes. Subsequently, the samples were analysed by ICP-OES after an acid microwave digestion (three parts hydrochloric acid (35 %) and one part nitric acid (65 %) at 200 °C).

At a first glance on the results, it becomes clear that there must be something wrong with the results for Cr and Ni because in all particle classes, the concentration of those components is much higher than in the original fly ash. Some contamination of the sample with Cr and Ni must have happened during the analytical procedure. For the task of that study, this was not crucial because the concentrations of Cr and Ni in the fly ash sample were significantly below the legal limits. However, the identification of the source for the contamination of the samples in the analytical procedure is important. The contamination of samples in the preparation steps for trace element analysis and methods for avoiding such contamination are described in the literature (Cubadda et al. 2001, 2005; Dahlin et al. 2012; Evans et al. 2003; Hoenig 2001; Santos et al. 2002, 2008; Welna et al. 2011). According to these studies, grinding, milling and homogenization of solid samples are possible sources for the contamination of the samples. However, the dust samples have neither been ground nor homogenized. Therefore, another source must have caused the contamination of the sample. The aim of this study is to investigate and identify the source of the Cr and Ni contamination.

The primary study was carried out in 2007, and the survey for identification of the source of contamination was done in 2012, both at the University of Applied Sciences Upper Austria.

Materials and methods

Material balances with the available data of the fly ash were used for the evaluation of the whole separation process. The recovery rate R_i was calculated for each component according to Eq. (1). In this equation, F_j is the mass fraction of the Particle Class j in the fly ash and $c_{\mathrm{mi},j}$ is the mass concentration of the component i in the Particle Class j. The concentration of this component is the original fly ash sample is $c_{\mathrm{mi},0}$.

$$R_i = \frac{1}{c_{\mathrm{mi},0}} \cdot \sum_{j=1}^{N} c_{\mathrm{mi},j} \cdot F_j \quad (1)$$

The surplus of a component S_i results from Eq. (2).

$$S_i = R_i - 1 \quad (2)$$

For characterization of the behaviour of Cr and Ni during the combustion process, their equilibrium distribution between the different phases was calculated in dependence of the temperature. For this calculation, the program HSC Chemistry® 5.1 from Outotec Oy, Pori, Finland was used. The typical composition for the biomass combustion off-gas was chosen with the following mole fractions: N_2: 71 %; O_2: 7 %; CO_2: 12 % and H_2O: 10 %. For the fly ash, a simplified composition was assumed with 64 % CaO, 32 % SiO_2, 2 % KCl and 2 % C. Additionally, a concentration of Cr and Ni of 60 mg/kg was considered.

Table 2 Calculated recovery rates for various heavy metals

	Recovery factor	Surplus
As	1.13	0.13
Cd	1.03	0.03
Co	1.10	0.10
Cr	4.63	3.63
Cu	1.03	0.03
Ni	3.34	2.34
Pb	0.98	−0.02
Zn	1.02	0.02

Results and discussion

Evaluation of the results of the analytical procedure

For the heavy metals partly volatile at combustion conditions, for example, Pb and Zn, the concentration in the fine particle classes is also much higher than in the fly ash, but this is compensated by a much lower concentration in the coarse classes. The concentration of components, which are non-volatile at process temperature, like Co, is quite even in all particle classes.

The calculated recovery rates for the various heavy metals and the surplus are shown in Table 2. As to be expected, the recovery rates are close to 1.0 for most components. That means that practically the same mass of those components that has been in the original fly ash was found in the produced particle classes altogether. However, for Cr and Ni, the recovery rates are much higher. This clearly shows that the sample has been contaminated with Cr and Ni during the analytical procedure.

Identification of the source of sample contamination

Because only the two elements Cr and Ni are involved in sample contamination, the most likely source of contamination would be some stainless steel where those components are present at higher concentrations. As possible pathways, a corrosive reaction with some stainless steel parts during the acid microwave digestion for the chemical analysis and erosion of stainless steel equipment during classification were identified.

For two reasons, corrosive reactions during acid sample digestion are very unlikely the source of the contamination. First, the Cr and Ni concentration in the original fly ash sample, which has been digested and analysed applying the same procedure, showed no significant deviation from the usual values for this fly ash. For comparison, the calculated average and the standard deviation for three other fly ash samples collected in the heating season 2006/07 (Lacher 2007) are shown in Table 3. And second, in a post-measurement inspection of the digestion equipment, no stainless steel parts, which can come in contact with the acid, could be found.

Table 3 Average heavy metals concentrations in the fly ash

	Average mg/kg (d.w.)	Standard deviation mg/kg (d.w.)	Relative standard deviation in %
As	17.9	9.4	52
Cd	25.3	6.6	26
Co	14.0	3.2	23
Cr	50.2	14.1	28
Cu	136	8.7	6
Ni	53.7	12.0	22
Pb	98.4	62.3	63
Zn	3,070	324	11

Erosion as the source of sample contamination is, however, much easier imaginable because several parts of the classification equipment are made of stainless steel. The ratio of the surplus of Cr and Ni helps to support this assumption. The calculated value for the ratio $S_{\mathrm{Cr}}/S_{\mathrm{Ni}}$ is about 1.6. According to Hosokawa Alpine, the manufacturer of the classifier, the impeller of the classifier is made of stainless steel, grade 1.4308 (EN 10027-2) and the cyclone for the collection of the fine fraction is made of stainless steel, grade 1.4541 (EN 10027-2). The concentrations of Cr and Ni in these materials are 18 and 10 %, respectively. This gives a ratio of Cr to Ni of 1.8, which is similar to the ratio of the surplus of these components.

The results of the equilibrium composition calculations are shown in Fig. 1. It is evident that at the combustion temperature of 820 °C, only a small fraction of Cr and Ni is present in the gaseous phase. Therefore, only very little deposition of Cr and Ni can happen during the cooling of the off-gas and for the further considerations the concentration of Cr and Ni can be assumed to be independent of the particle size. The increase in the Cr and the Ni concentration $\Delta c_{\mathrm{mi,j}}$ can then be calculated by $\Delta c_{\mathrm{mi},j} = c_{\mathrm{mi},j} - c_{\mathrm{mi},0}$.

In Fig. 2, the concentration increase in Cr and Ni in the various particle classes is shown to be dependent on the mass median diameter of the particle size class. It is noticeable that in the fine particles of Particle Class 1, the concentrations are only a bit above the concentration in the fly ash, whereas for Particle Class 2, the concentration increase is much higher. From Particle Class 2 to Particle Class 6, the concentration increase diminishes. A possible explanation of that effect is the following: in the first classification run, the particles of Particle Class 1 passed the impeller of the classifier with little contact with the impeller, whereas for the

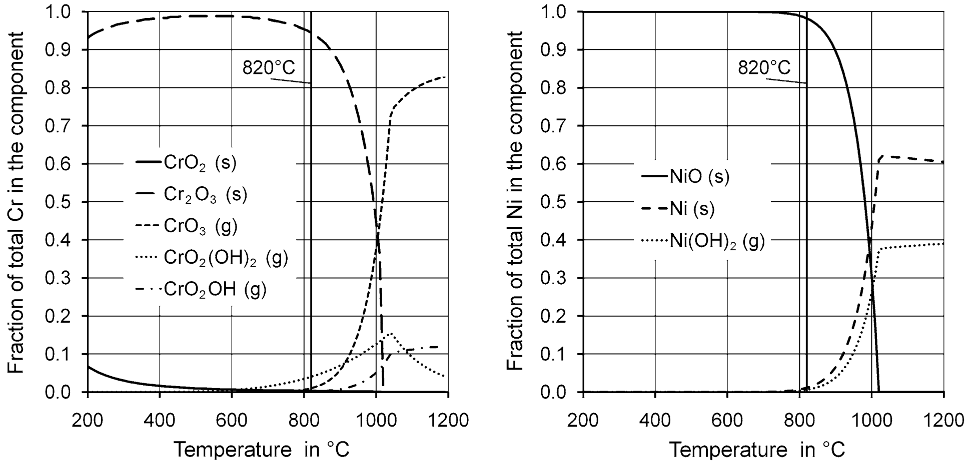

Fig. 1 Calculated equilibrium composition of Cr (*left*) and Ni (*right*) containing components

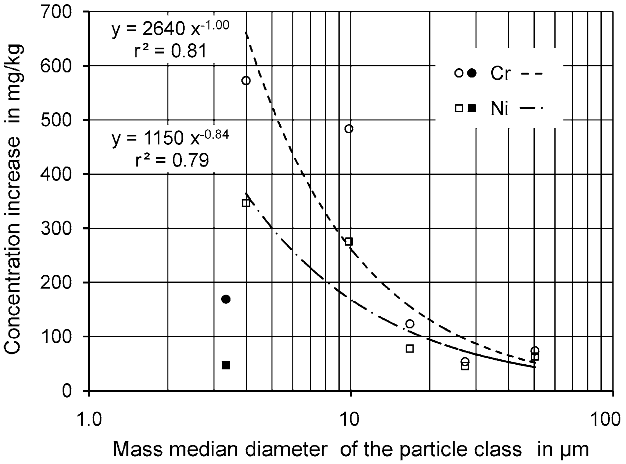

Fig. 2 Concentration increase in dependence of the particle size (the *full symbols* are for the first classification run)

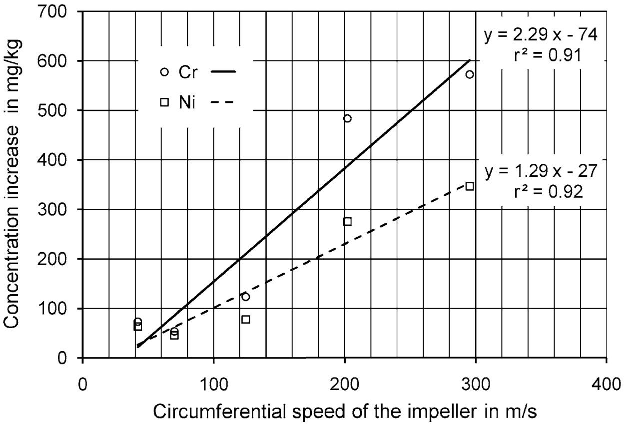

Fig. 3 Concentration increase in the fraction passing the impeller in dependence of the circumferential speed of the impeller during the previous classification run

particles that were a little too big for passage, the likelihood for collision with the impeller during their rejection was increased. As the speed of the impeller was highest in this classification run, the erosion caused by those collisions was high. Particles which are much bigger did not come into contact with the impeller at all. The smaller fraction of the particles that were rejected in the first classification run passed the impeller in the second classification run and subsequently was collected as Particle Class 2, and consequently, the concentration increase for Cr and Ni in this particle class is much higher. The same procedure took place in each classification run, but as the speed of the impeller was reduced from one classification run to the next, the erosion by the particles coming in contact with the impeller decreased each run. Therefore, from particle class to particle class, the concentration increase for Cr and Ni is always less. The results of a linear regression of the data for of Particle Class 2 to Particle Class 6 (empty symbols) are also shown in Fig. 2. The coefficient for determination (r^2) is 0.81 for Cr and 0.79 for Ni.

The concentration increase in a particle class depends on the maximum circumferential speed of the impeller (w) in the previous classification run. This is shown in Fig. 3. The coefficient for determination (r^2) is quite high for both components.

For the estimation of the influence of erosion in the cyclone and the connecting tube, the gas velocities, which were constant for all classification runs, were calculated. In the connecting tube to the cyclone, the gas velocity was 17 m/s. The maximum circumferential gas velocity in the cyclone was calculated according to Muschelknautz and Trefz (2002). In comparison with the maximum circumferential speed of the impeller, the value for the maximum circumferential gas velocity of 22 m/s and the gas velocity in the tube are low. Therefore, it can be assumed that the contribution of erosion in the cyclone to the contamination of the sample is relatively low.

Conclusion

The source for the contamination of a classified fly ash sample with Cr and Ni was investigated. It was found that the ratio of Cr to Ni in the calculated surplus contamination of the samples was equal to the Cr to Ni ratio in typical stainless steel grades, which were, for example, also used as construction material for the used classifier. Corrosion of stainless steel, for example, during the acid digestion of the samples was very unlikely the source of the contamination because the analysis of the fly ash sample, that was treated in the same way as the classified samples, showed no increase in the Cr and Ni concentration. Erosion in the classifier, especially at the impeller, was found to be the most likely source for the contamination of the samples.

For classification of granular samples in the 1–100 µm size range, air classifiers can be used. However, if the classified samples have to be analysed for Cr and Ni, a classifier with an impeller made of another material than stainless steel or coated with another material should be used. This is especially important when the expected concentrations or Cr and Ni are below 1–10 g/kg.

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