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Characterisation and on-line measurements of ashes – Continuous leaching and analysis of ashes

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Key words: Ash leaching, online analysis, critical elements

Summary

A procedure for continuous analysis of elements leached from fly ashes using different leachates has been developed. This method enables for fast analysis and determination of elements leached and the leaching rates. A flow through reactor is used in the procedure, however various reactor types can be used. Using the flow through reactor, the leachate is pumped through a plug of ash and the elements leached are analyzed using ICP-OES. Different solvents can be used in the procedure. Additionally the temperature in the reactor can be adjusted. The method enables for rapid testing of different parameters with the on-line analysis of the leached elements.

Three fly ashes, two from a BFB boiler and one from a CFB boiler, were studied with the method. The main focus was on the leaching of Co, Cu, and Sb. However, 20 elements can be simultaneously analyzed every 16 s. Water was used as the first leachate to determine the water soluble elements. 0.50 g of salt was used in the experiments and the flow through the ash was 0.6 ml/min. After 30 min of leaching with water, a solution of 5 M HNO_3 was pumped through the ash for 2 h 10 min. Co, Cu, and Sb were leached only when HNO_3 was used as solvent. The leaching rate was faster during the first 30 to 60 min of the leaching procedure. For example, over 50% of Co, Cu, and Sb in BFB2 ash were leached during the first 30 minutes with HNO_3 as solvent.

Helsinki, september 2015

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1. Method

1.1. Procedure for continuous leaching and analysis of ashes

A procedure for continuous analysis of elements leached from fly ashes using different leachates has been developed. This method enables for fast analysis and determination of elements leached using different solvents. A scheme of the procedure is shown in Figure 1. Similar setups have been used before in chemical fractionation studies of fuels [1][2].

A flow through reactor was used in the procedure, however various reactor types can be used. Using the flow through reactor, the solvent is pumped through a plug of ash and the elements leached are analyzed continuously using ICP-OES. The ash is kept in place with quarz wool and tefon filters were used to avoid particles from escaping the reactor. Water was used as the first leachate to determine the water soluble elements. 0.50 g of ash was placed in the reactor in the experiments and the flow through the ash was 0.6 ml/min. A total of 20 elements are analyzed every 16 s, those are: Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, P, Pb, S, Sb, Se, Si, V, and Zn. After 30 min of leaching with water, a solution of 5 M HNO_3 was pumped through the ash for 2 h 10 min. The weight loss during the leaching procedure was determined and the remainings of the ash was analyzed using SEM-EDX. For the weight loss determination the ash was dried in an oven at 105°C for 24h.

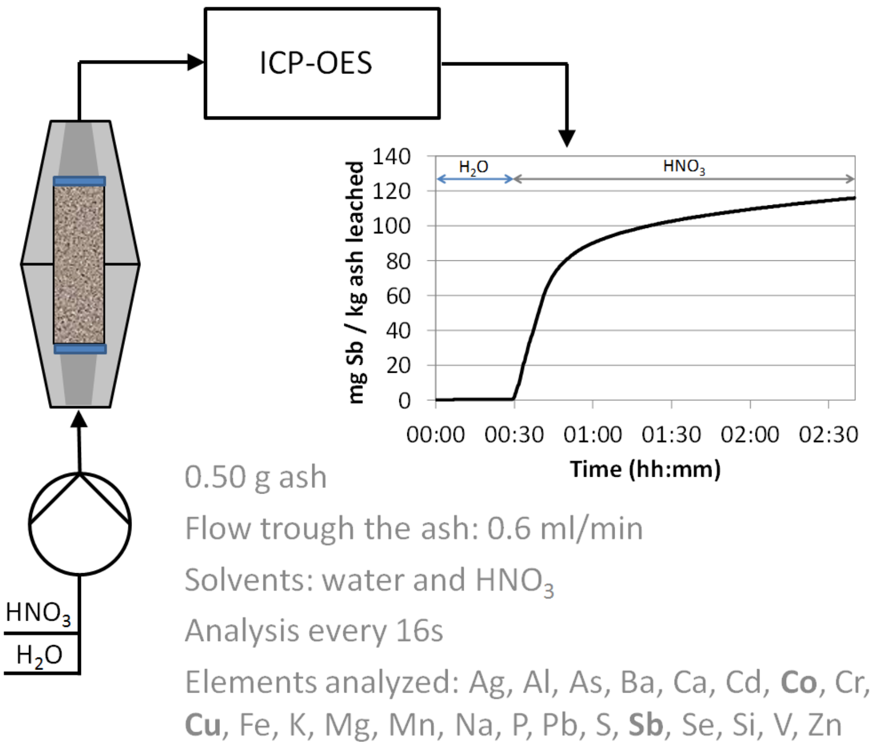

Figure 1. Scheme of the procedure for continuous leaching and analysis of ashes using a flow through reactor and ICP-OES.

Pre-testing was conducted to find the best wavelength for each element to avoid any overlapping of the different elements. The wavelengths used in the ICP-OES are given in Table 1.

Table 1. Wavelengths used in the ICP-OES analyses.

Element	Wavelength (nm)
Silver (Ag)	328.068
Aluminium (Al)	396.153
Arsenic (As)	193.696
Barium (Ba)	233.527
Calcium (Ca)	317.933
Cadmium (Cd)	214.44
Cobol (Co)	228.616
Chromium (Cr)	283.563
Copper (Cu)	324.752
Iron (Fe)	238.204
Potassiu (K)	766.49
Magnesium (Mg)	285.213
Manganese (Mn)	257.61
Sodium (Na)	589.592
Phosphorus (P)	213.617
Lead (Pb)	220.353
Sulfur (S)	181.975
Antimony (Sb)	206.836
Selenium (Se)	196.026
Silicon (Si)	251.611
Vanadium (V)	290.88
Zinc (Zn)	213.857

1.2. Ashes tested

Three ashes were studied with the leaching method: two baghouse filter ashes from a bubbling fluidized bed boiler and one ESP ash from a circulating fluidized bed boiler. Elemental analyses of the ashes were made before the leaching tests. Emphasis was laid on Co, Cu, and Sb in the tests.

2. Results

2.1. BFB1 baghouse ash

2.1.1. Ash analyses

BFB1 baghouse ash contained relatively low amounts of the valuable elements: 20 mg/kg Co, 27 mg/kg Sb, and 426 mg/kg Cu on a dry basis. This ash was from the co-combustion of bark, wood, sludge, and solid recovered fuels. The elemental analysis of BFB1 ash is shown in Figure 2. Pictures of the ash before and after the leaching procedure are shown in Figure 3.

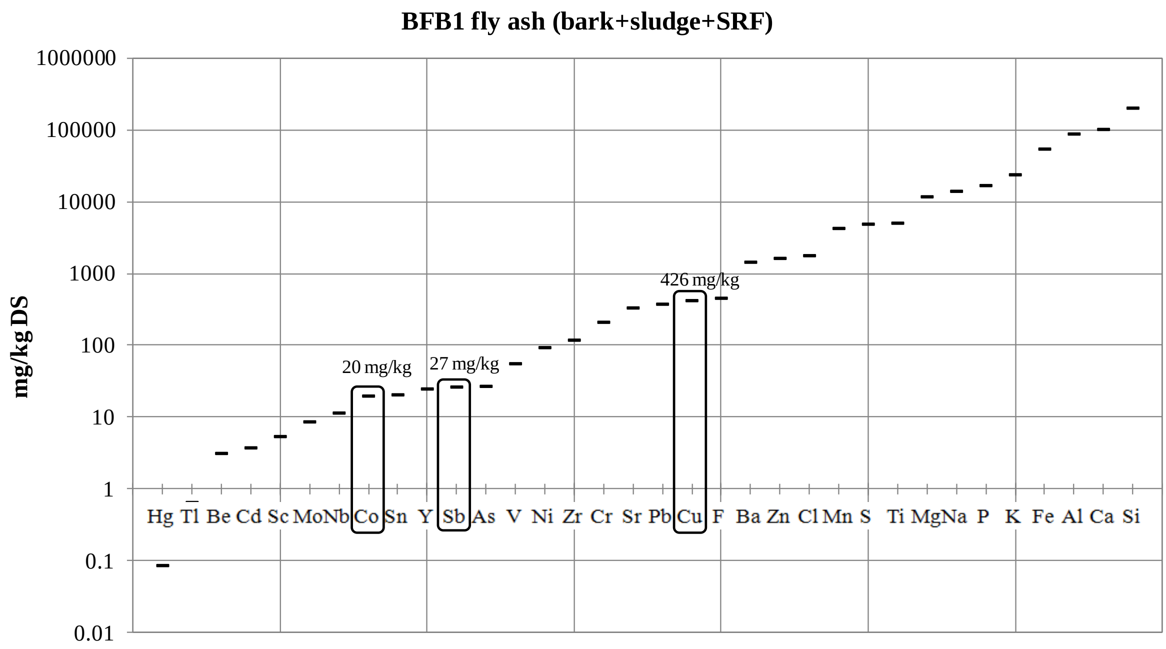

Figure 2. Elemental composition of the BFB1 baghouse ash. Note the logarithmic scale.

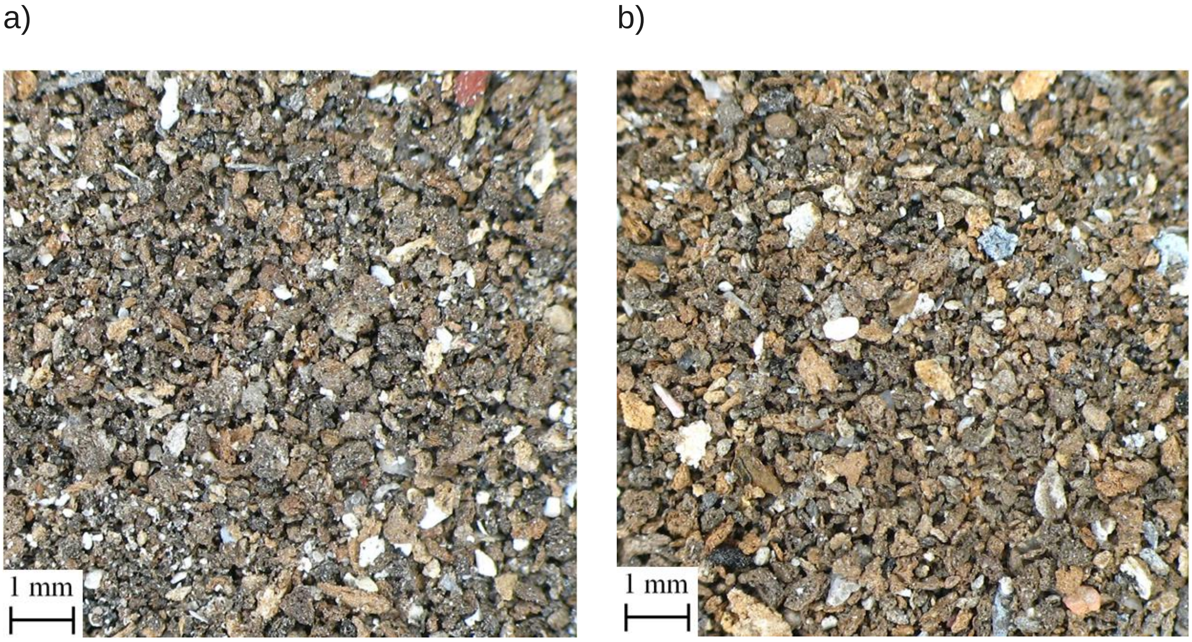

Figure 3. BFB 1 fly ash before (a) and after (b) leaching.

2.1.2. Leaching results

The leaching results of Co, Cu, and Sb are shown in Figure 4. The figure shows the cumulative leaching of each element calculated as mg of element leached per kg of ash. None of the elements were leached with water. Leaching only occurred when 5M HNO_3 was used as solvent. During the first 30 minutes with HNO_3 the leaching was faster. The percentage of each element leached compared to the ash analyses were: 21% of Co, 62% of Cu, and 44% of Sb. The total weight loss during the leaching experiment was 39%.

Other major elements leached during the leaching procedure are shown in Figure 5. Water soluble Ca, S, Na and K were leached during the first 30 min with water. The Na curve was saturated in the beginning of the leaching with water and both Na and K were saturated when HNO_3 was added. The leaching was enhanced with HNO_3 as solvent, and Al, Fe, Mg, and Zn were also leached.

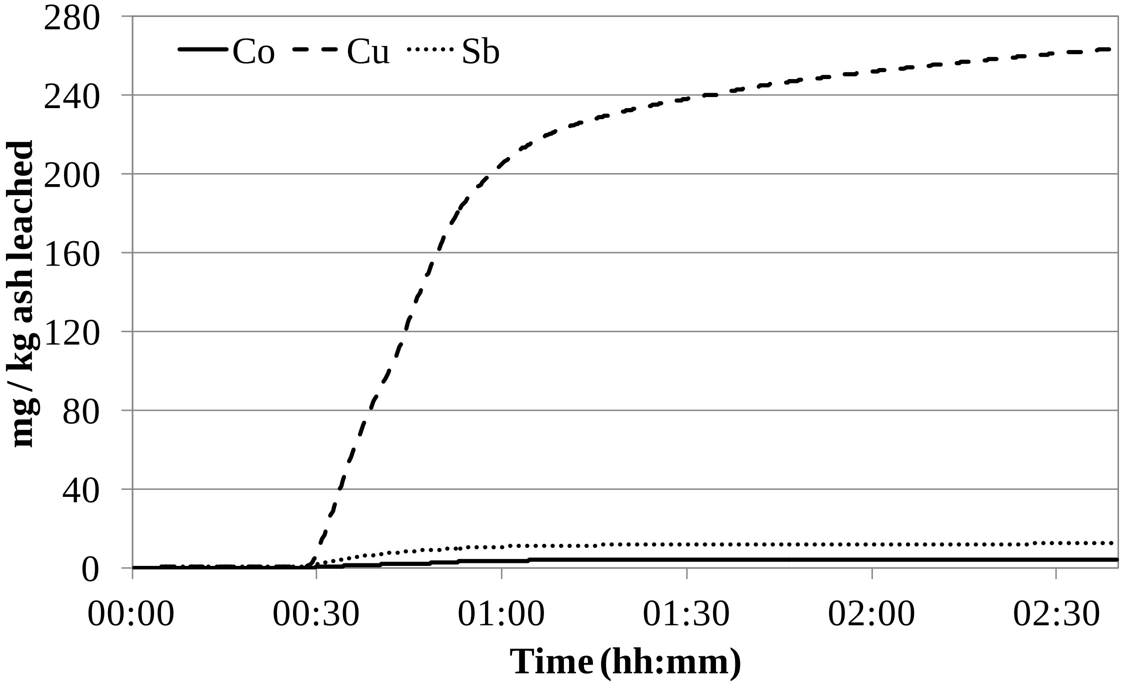

Figure 4. Leaching results of Co, Cu, and Sb from BFB1 ash. The ash was first leached with water and after 30 min 5M HNO_3 was used as solvent.

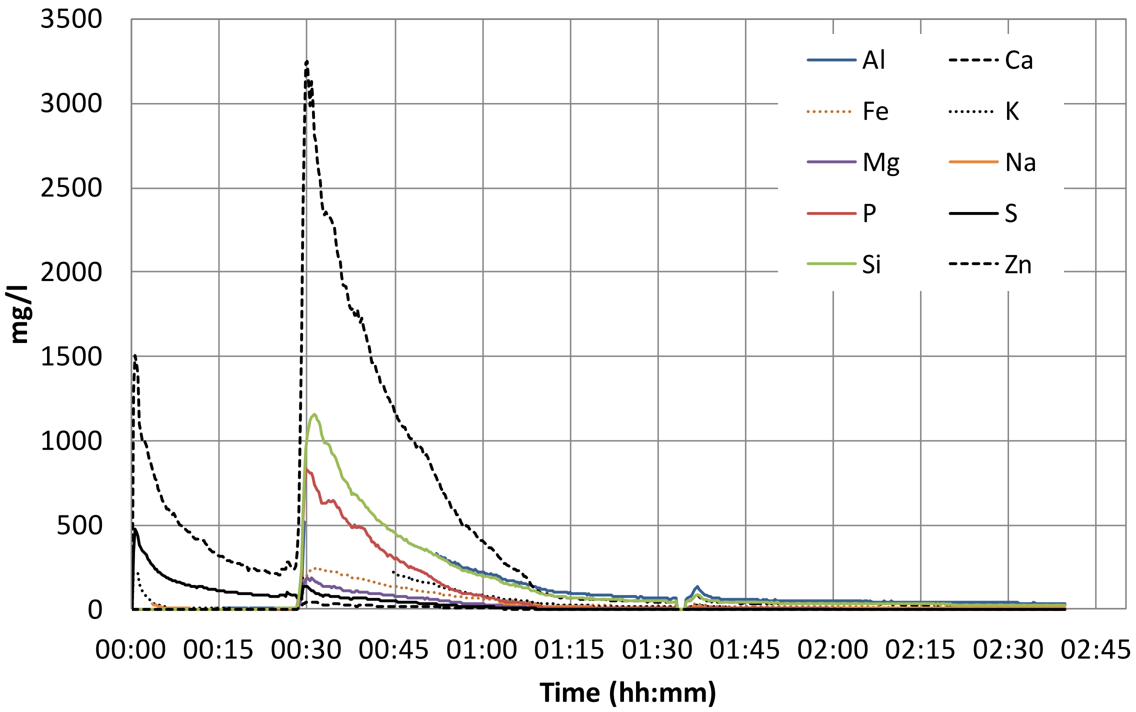

Figure 5. Other major elements leached as mg/l. The ash was first leached with water and after 30 min 5M HNO_3 was used as solvent.

2.2. BFB2 baghouse ash

2.2.1. Ash analyses

BFB2 baghouse ash contained the highest amounts of the valuable elements out of the three ashes studied: 30 mg/kg Co, 173 mg/kg Sb, and 2170 mg/kg Cu on a dry basis. This ash was from the combustion of demolition wood in a bubbling fluidized bed boiler. The elemental analysis of BFB2 ash is shown in Figure 6. Pictures of the ash before and after the leaching procedure are shown in Figure 7 A and B. It can clearly be seen that the particle size was much smaller than for the BFB1 ash.

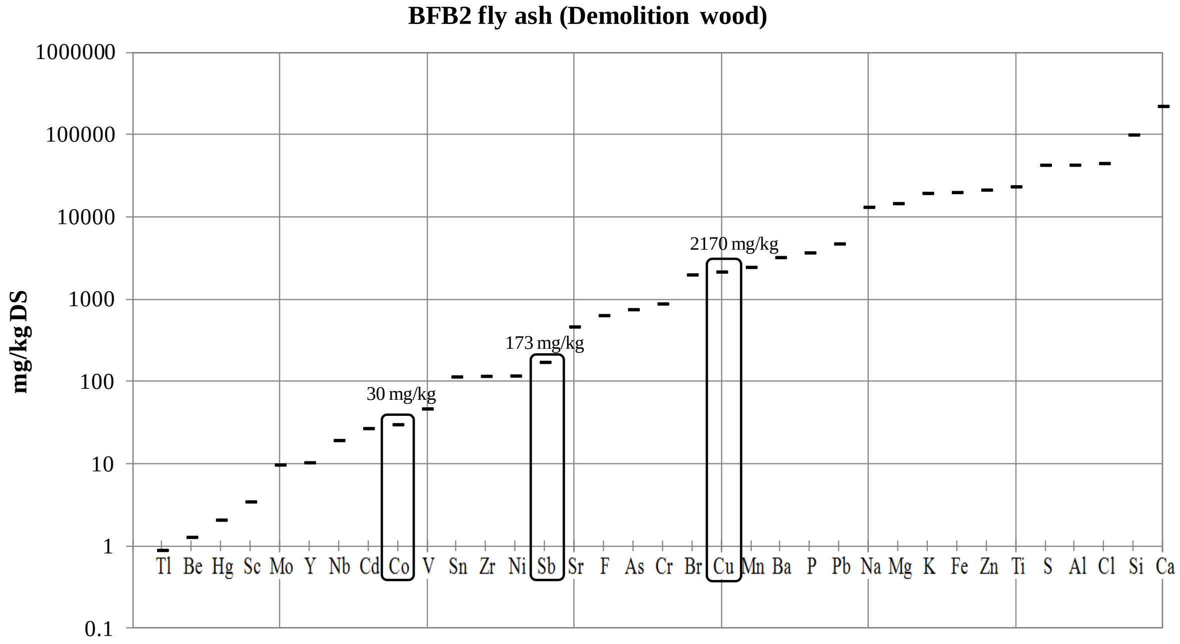

Figure 6. Elemental composition of the BFB2 baghouse ash. Note the logarithmic scale.

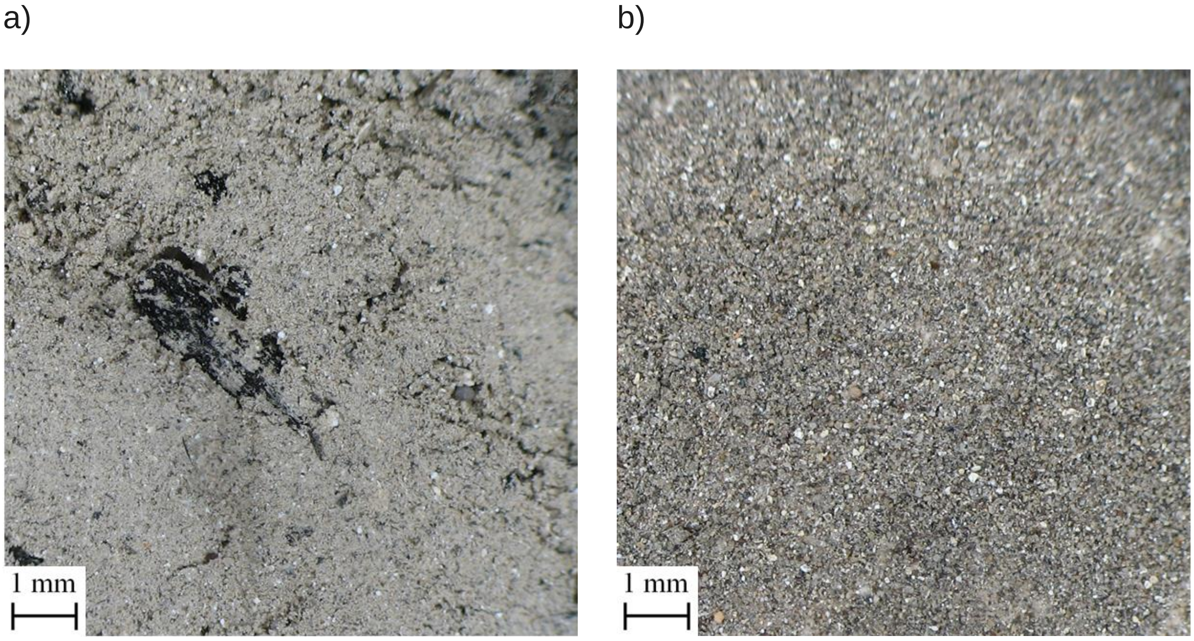

Figure 7. BFB2 fly ash before (a) and after leaching (b).

2.2.2. Leaching results

The leaching results of Co, Cu, and Sb for the BFB2 ash are shown in Figure 8. The figure shows the cumulative leaching of each element calculated as mg of element leached per kg of ash. None of the elements were leached with water. Leaching only occurred when 5M HNO_3 was used as solvent. During the first 30 minutes with HNO_3 the leaching was faster. The percentage of each element leached compared to the ash analyses were: 53% of Co, 68% of Cu, and 86% of Sb. 70% of the total weight was leached during the procedure. This is much higher than for the BFB1 ash and may be attributed to the difference in particle size distribution.

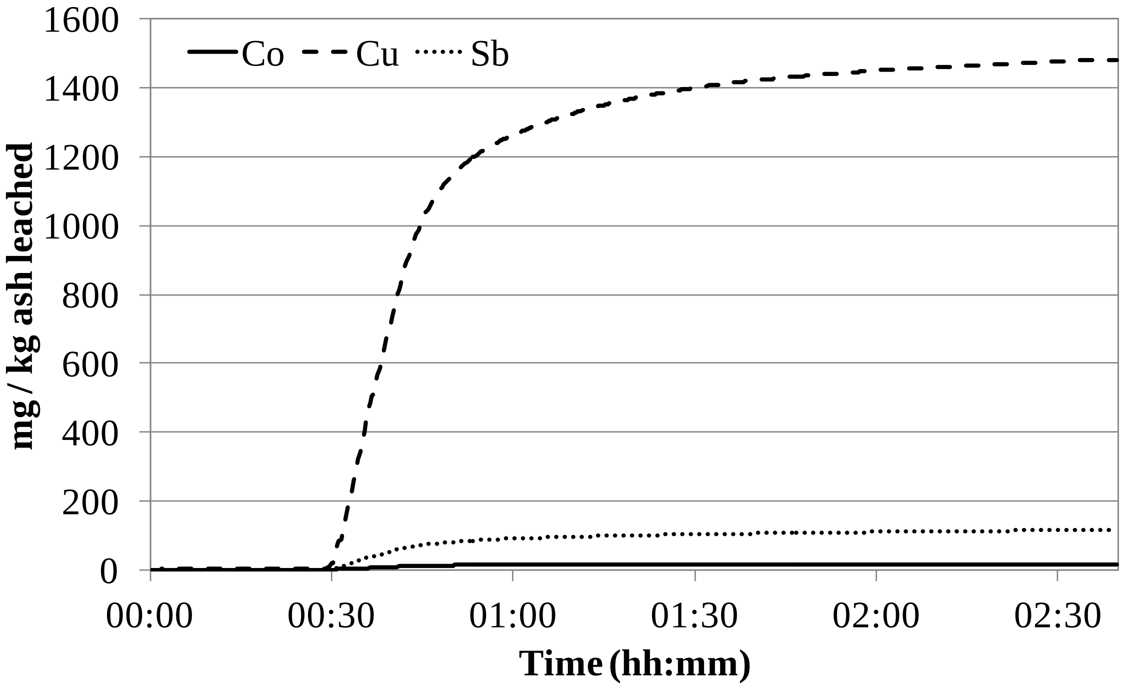

Figure 8. Leaching results of Co, Cu, and Sb from BFB2 ash. The ash was first leached with water and after 30 min 5M HNO_3 was used as solvent.

Other major elements leached during the leaching procedure are shown in Figure 9. Water soluble Ca, S, and K were leached during the first 30 min with water. The potassium curve was saturated the first 10 minutes. The leaching was enhanced with HNO_3 as solvent, and Al, Fe, Mg, and Zn were also leached.

SEM-EDX analyses were made on the ash before and after the leaching procedure, and the results are shown as molar percentage in Figure 10. The remaining ash after the leaching is enriched in Al, Fe, Si, Ti, and Zn. Most of the Cu, S, and Cl were leached out from the ash. Co and Sb were below the detection limit for SEM-EDX.

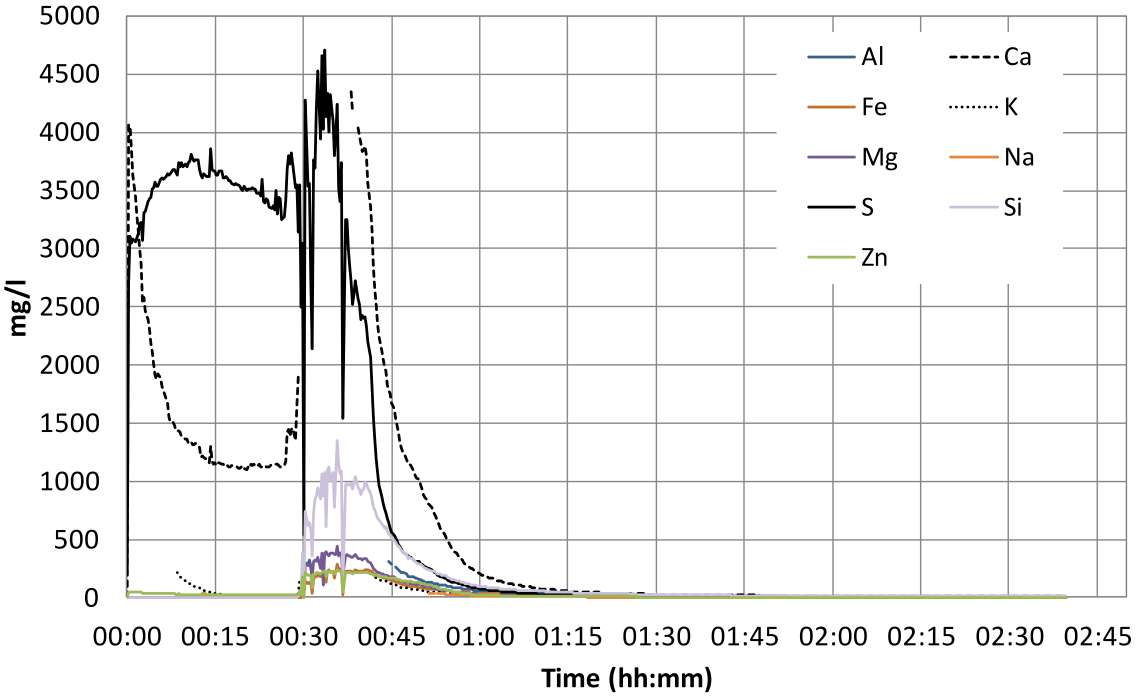

Figure 9. Other major elements leached as mg/l. The ash was first leached with water and after 30 min 5M HNO_3 was used as solvent.

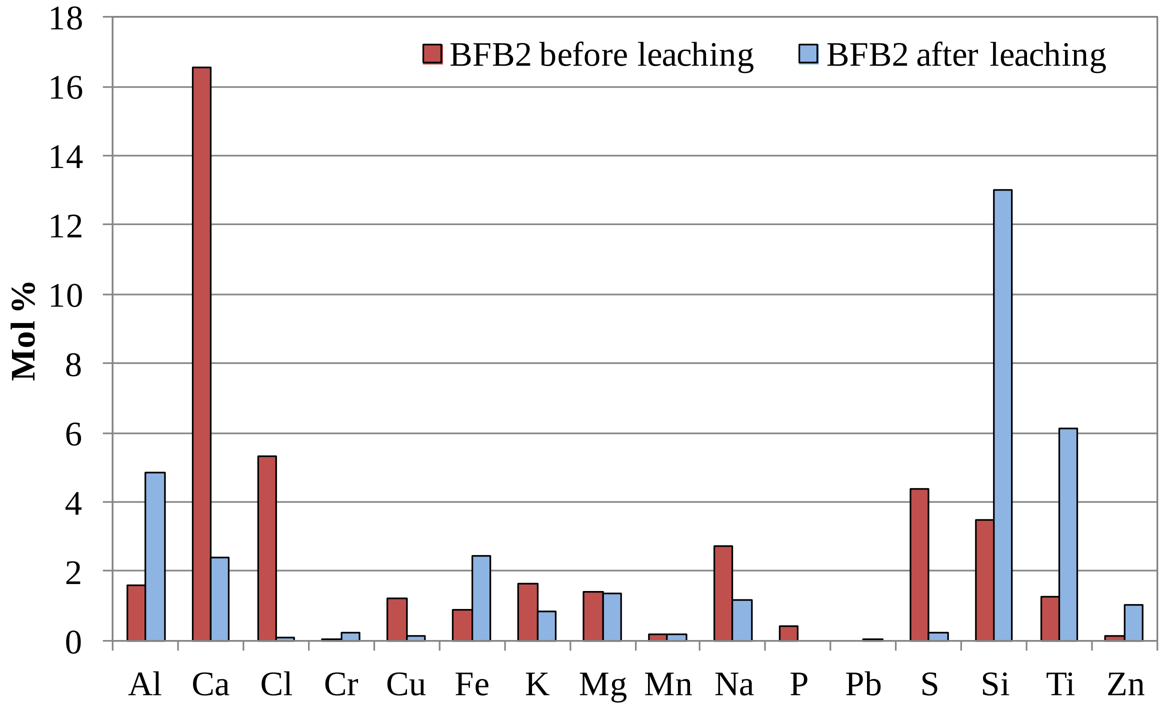

Figure 10. SEM-EDX of the ash before and after the leaching procedure.

2.3. CFB ESP ash

2.3.1. Ash analyses

The third ash was an ESP ash from a circulating fluidized bed boiler. The amounts of the three elements in the ash were: 29 mg/kg Co, 135 mg/kg Sb, and 1410 mg/kg Cu on a dry basis. The elemental analysis of CFB ash is shown in Figure 11. Pictures of the ash before and after the leaching procedure are shown in Figure 12 A and B. Most of the ash was leached during the procedure. The remaining part contained some unburned carbon as can be seen in the after picture.

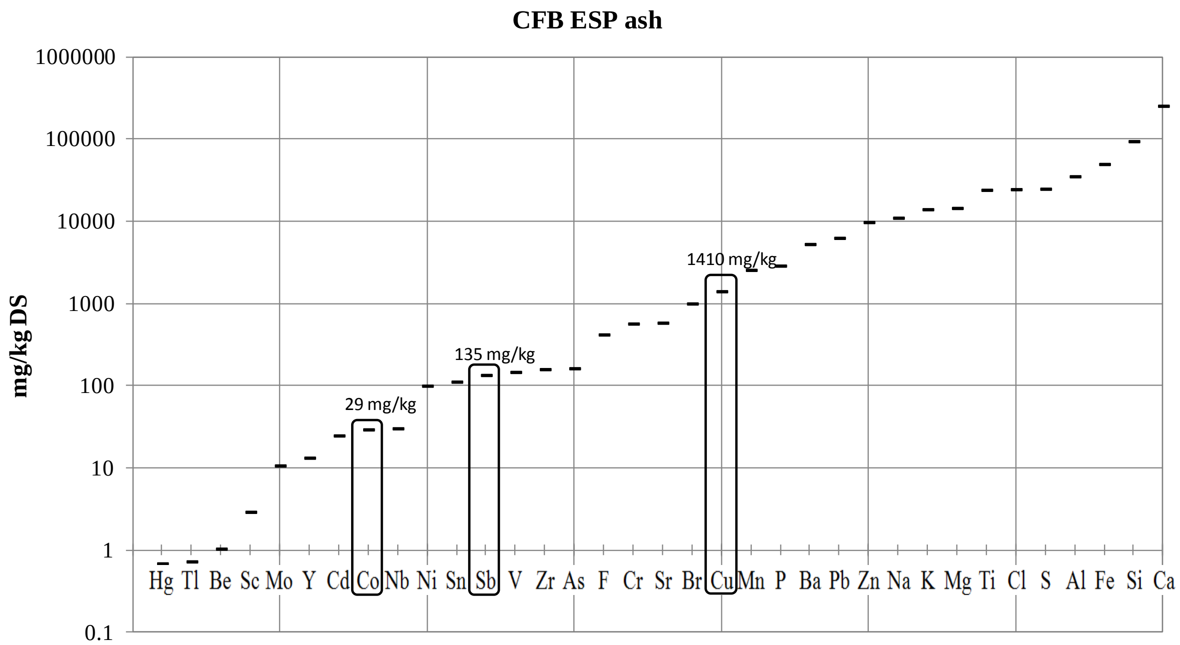

Figure 11. Elemental composition of the CFB ESP ash. Note the logarithmic scale.

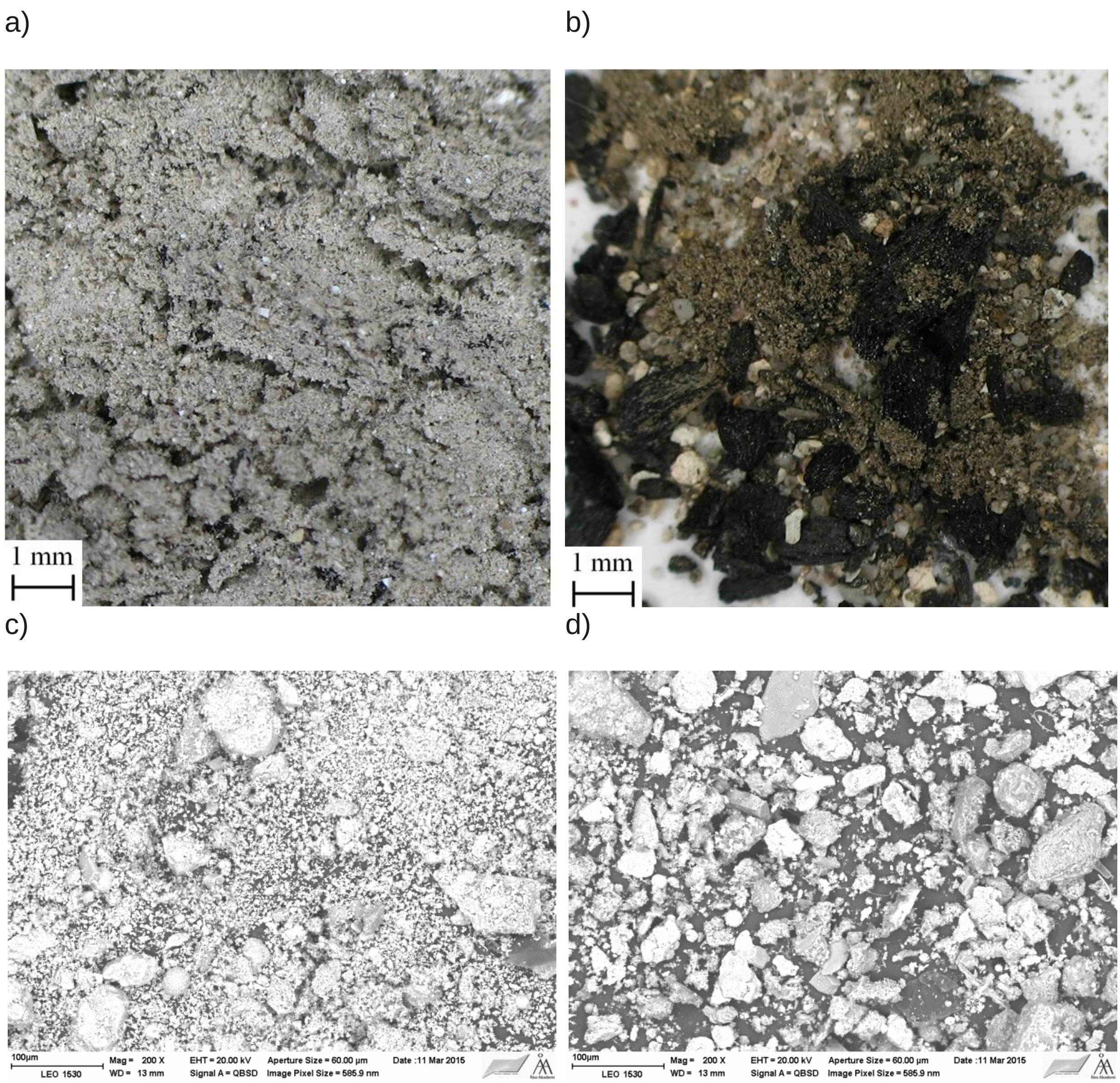

Figure 12. CFB ESP ash before (a and c) and after leaching (b and d).

2.3.2. Leaching results

The leaching results of Co, Cu, and Sb for the CFB ash are shown in Figure 13. The figure shows the cumulative leaching of each element calculated as mg of element leached per kg of ash. Again, none of the elements were leached with water. Leaching only occurred when 5M HNO_3 was used as solvent. During the first 60 minutes with HNO_3 the leaching was faster, however, much slower than for the BFB ashes. No detectable Co was leached during the procedure. The percentage of each element leached compared to the ash analyses were: 0% of Co, 44% of Cu, and 53% of Sb. 66% of the total weight was leached during the procedure.

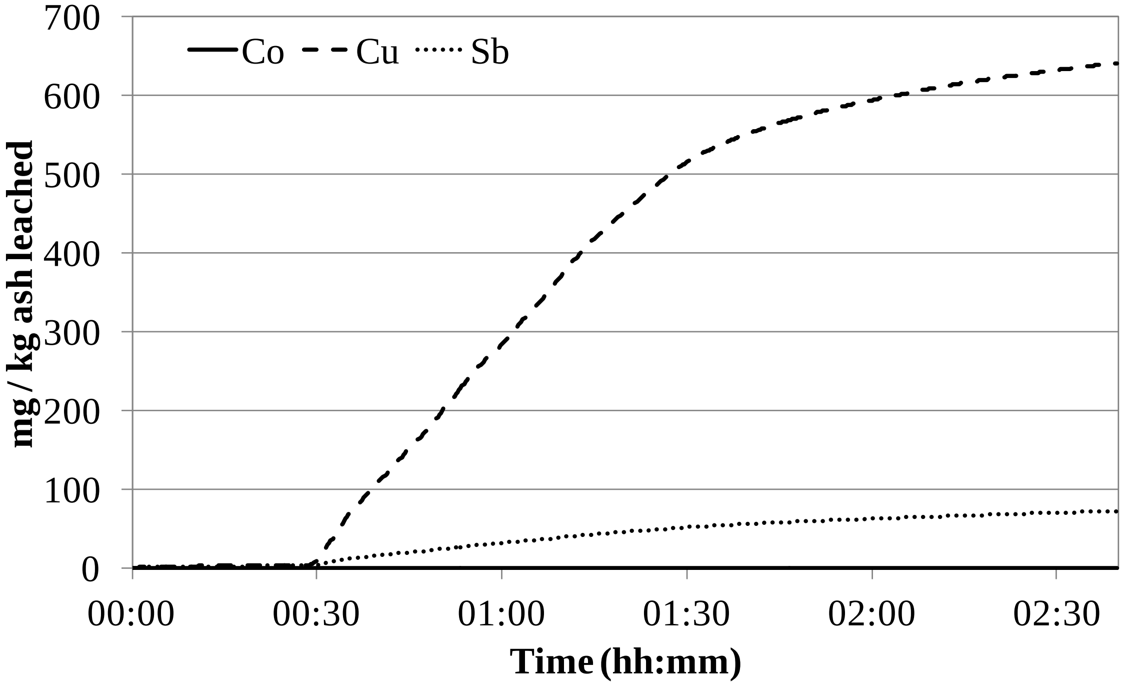

Figure 13. Leaching results of Co, Cu, and Sb from CFB ash. The ash was first leached with water and after 30 min 5M HNO_3 was used as solvent.

3. Summary

The cumulative leaching curves for Cu, Co, and Sb, as mg of the element leached per kg of ash leached, are shown in Figures 14-16. The leaching rate is faster for BFB2 ash. Most of the three elements are leached in the first 30 minutes with HNO_3.

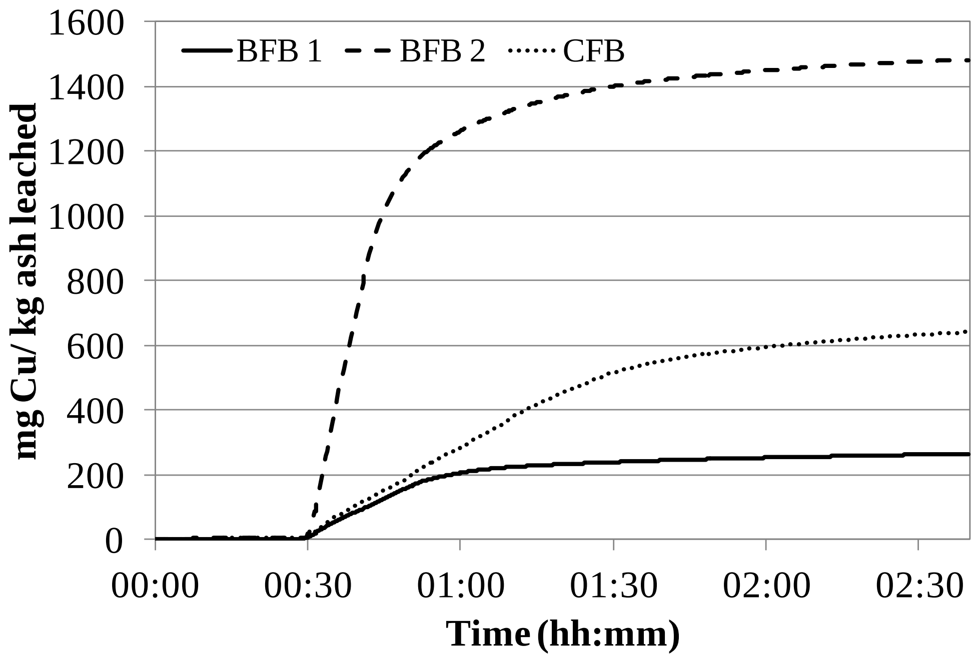

Figure 14. Leaching curves for Cu for the three ashes.

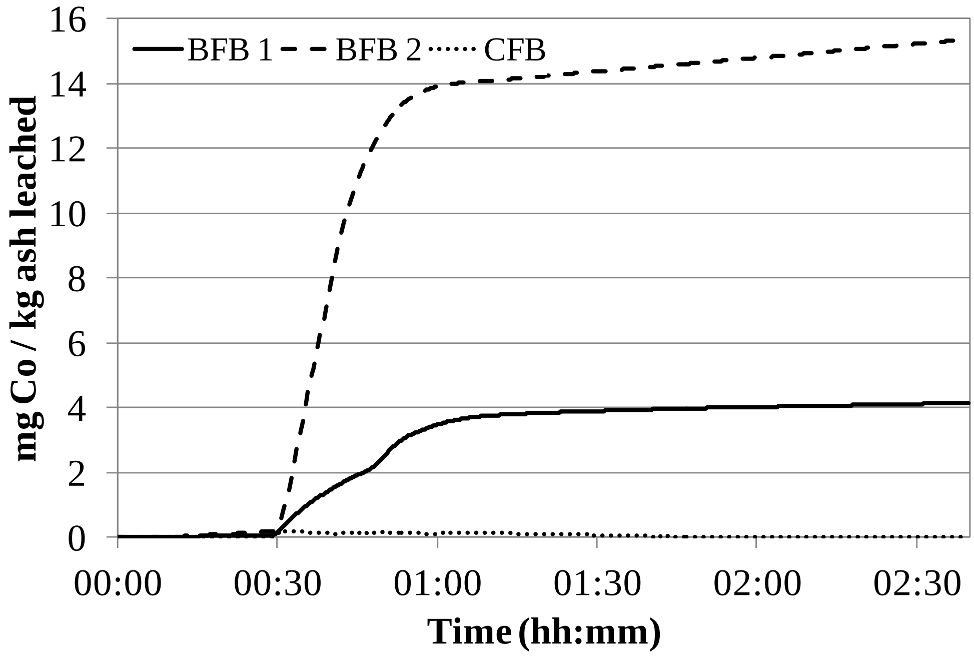

Figure 15. Leaching curves for Co for the three ashes.

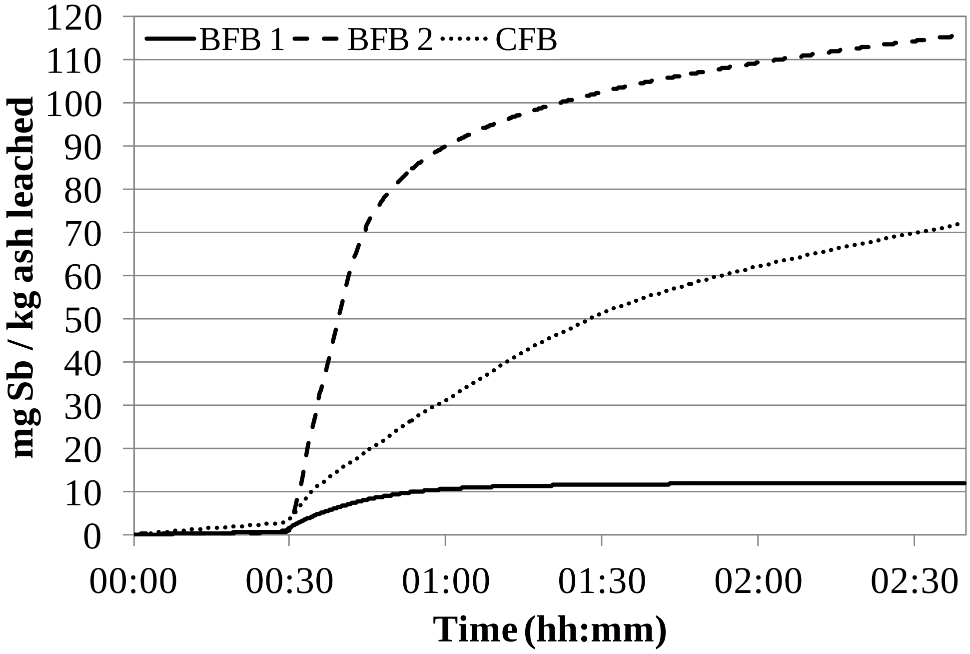

Figure 16. Leaching curves for Sb for the three ashes.

The BFB2 ash showed the highest leachability of Co, Cu, and Sb of the three ashes, which can be seen in Figure 17. This may have to do with the particle size distribution and how these elements were bound in the ash. The total leached material of the three ashes is shown in Figure 18. The BFB 2 ash showed the highest leachability.

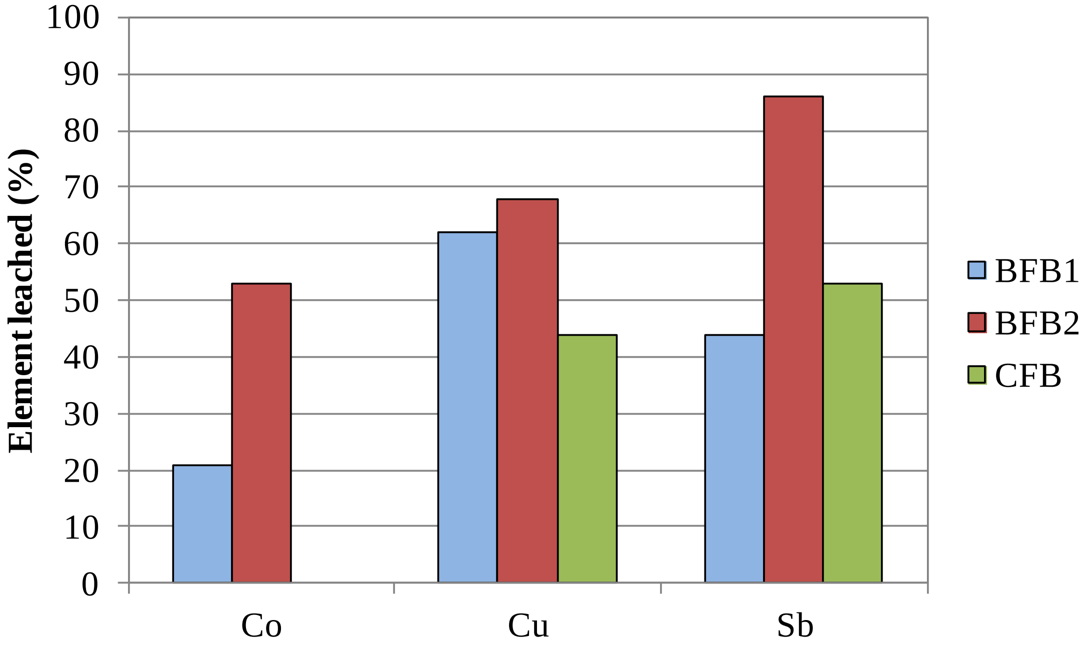

Figure 17. Co, Cu, and Sb leached during the leaching procedure.

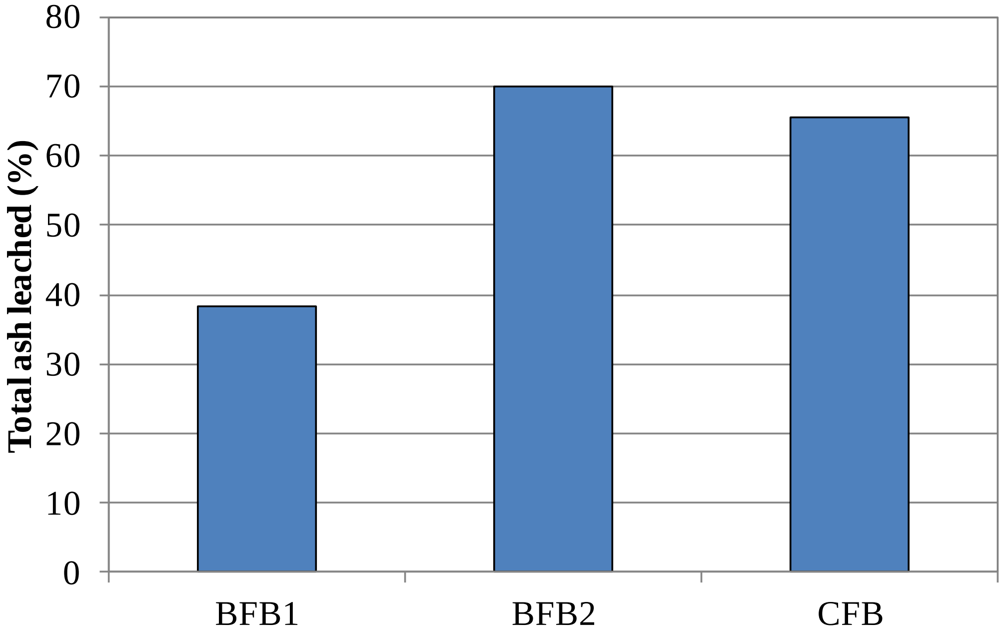

Figure 18. Total ash leached for the three ashes.

4. Conclusions

A procedure for continuous analysis of elements leached from fly ashes using different leachates has been developed. This method enables for fast analysis and determination of elements leached and the leaching rates. A flow through reactor is used in the procedure, however various reactor types can be used. Using the flow through reactor, the leachate is pumped through a plug of ash and the elements leached are analyzed using ICP-OES. Different solvents can be used in the procedure. Additionally the temperature in the reactor can be adjusted. The method enables for rapid testing of different parameters with the on-line analysis of the leached elements.

Three fly ashes, two from a BFB boiler and one from a CFB boiler, were studied with the method. The main focus was on the leaching of Co, Cu, and Sb. However, 20 elements can be simultaneously analyzed every 16 s. Water was used as the first leachate to determine the water soluble elements. 0.50 g of salt was used in the experiments and the flow through the ash was 0.6 ml/min. After 30 min of leaching with water, a solution of 5 M HNO_3 was pumped through the ash for 2 h 10 min. Co, Cu, and Sb were leached only when HNO_3 was used as solvent. The leaching rate was faster during the first 30 to 60 min of the leaching procedure. For example, over 50% of Co, Cu, and Sb in BFB2 ash were leached during the first 30 minutes with HNO_3 as solvent.

5. References

[1] Warunya Boonjob, Maria Zevenhoven, Paul Ek, Mikko Hupa, Ari Ivaska and Manuel Miro: Automatic dynamic chemical fractionation method with detection by plasma spectrometry for advanced characterization of solid biofuels, : J. Anal. At. Spectrom., 2012, 27, 841.

[2] Warunya Boonjob, Maria Zevenhoven, Mikko Hupa, Paul Ek, Ari Ivaska, Manuel Miró: Elucidation of associations of ash-forming matter in woody biomass residues using on-line chemical fractionation, Fuel 107 (2013) pp. 192–201.