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RESEARCH REPORT
NO 2.5-9
HELSINKI 2017

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Continuous leaching and analysis of ashes

Solution Architect for Global
Bioeconomy & Cleantech Opportunities

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ISBN 978-952-7205-22-8
ISSN XXXX-XXXX

PROCESS CHEMISTRY CENTRE

ÅBO AKADEMI UNIVERSITY

Arvi – Material Value Chain

2.5 Characterisation and on-line measurements of ashses

Continuous leaching and analysis of ashes

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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 was developed in the first part of the project. 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 wool buds and teflon 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 were analyzed every 16 s, those were: 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% 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.

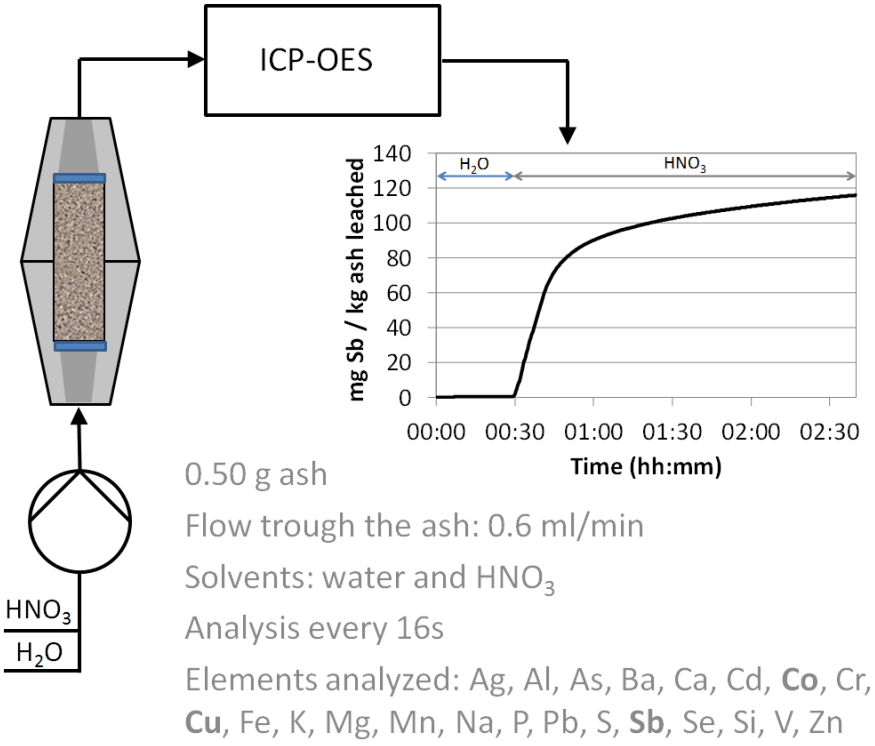


Figure 1. Scheme of the procedure for continuous leaching and analysis of ashes using a flow through reactor and ICP-OES.

Each element emits radiation at characteristic wavelengths in the plasma and the wavelengths used in this work are given in Table 1. These were chosen to avoid overlapping of the wavelengths in the complex matrix.

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

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

1.2. Ashes tested

Five ashes were tested and the Cu, Co, Sb contents are given in Table 2. The ashes originated from test runs made at the VTT CFB boiler. Ash T1 was from the co-combustion of demolition wood and plastic cables, and ashes T2-T5 were from combustion of demolition wood. The cyclone temperatures were adjusted for the different cases to: T1 and T2 650°C, T3 600°C, T4 500°C, and T5 450°C. The ashes were first leached with water for 30 min and then with a 5% HNO_3 water solution for 2 h and 10 min. Further, a sixth test was done with the ash designated T5 where it was leached for 24 h with water before the HNO_3 step .

Table 2. Cu, Co, and Sb contents in the ashes

Ash	Cu (mg/kg)	Co (mg/kg)	Sb (mg/kg)
CFB T1	990	48	390
CFB T2	1200	51	350
CFB T3	1400	53	400
CFB T4	1500	54	400
CFB T5	1400	52	370

2. Results

2.1. Ash T1

The leaching profiles for T1 are given in Figure 1. Some Sb is leached during the first 30 min. of water leaching. When HNO_3 leaching starts at 30 min., Cu and Co are also leached. The leaching rate is high for the first 15 min. with HNO_3. At the end of the test the total percentages of Co, Cu, and Sb leached were: 53, 40, and 50%. Table 3 shows microscope and SEM images of the ash before and after the leaching and the EDX results are presented in Figure 3. It can also be noted that all P, S, and Cl were leached out in the tests.

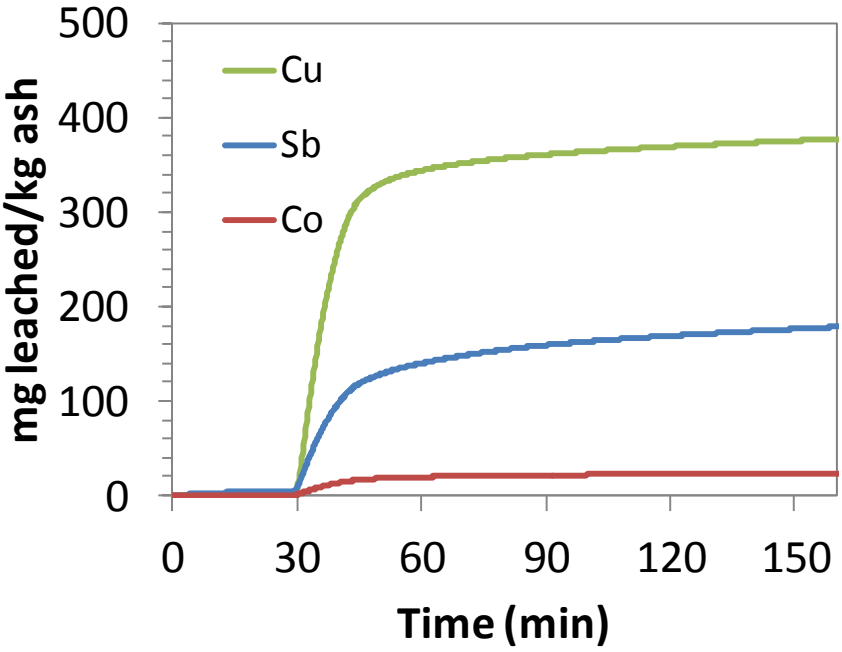
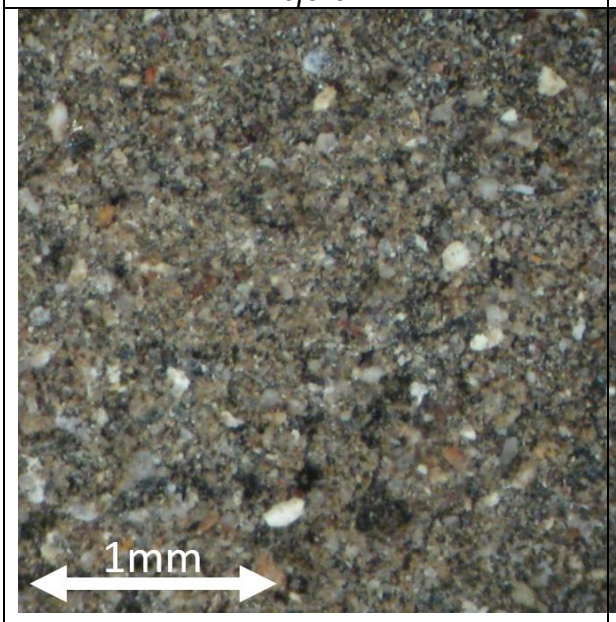
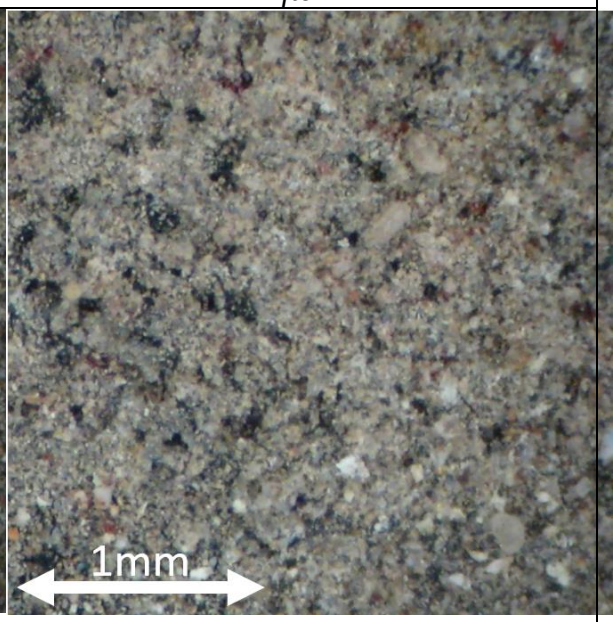
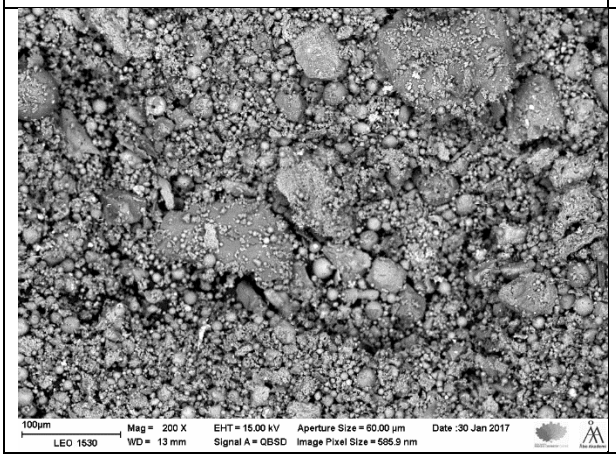
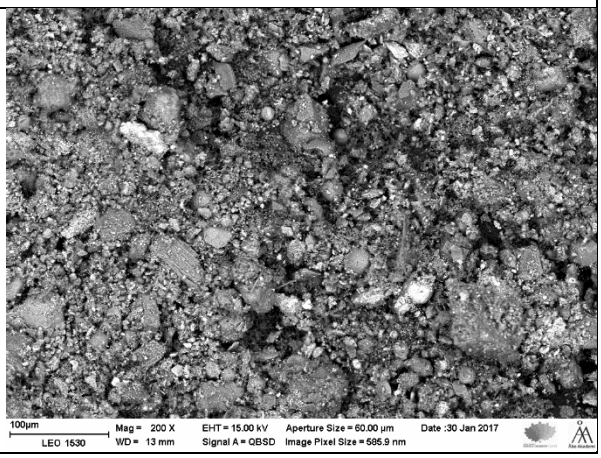


Figure 2. Leaching results of Co, Cu, and Sb of T1 ash. The ash was leached with water for the first 30 min and then with a 5% HNO_3solution.

Table 3. Microscope and SEM pictures of T1 ash before and after the leaching procedure.

Before	*After*
	
	

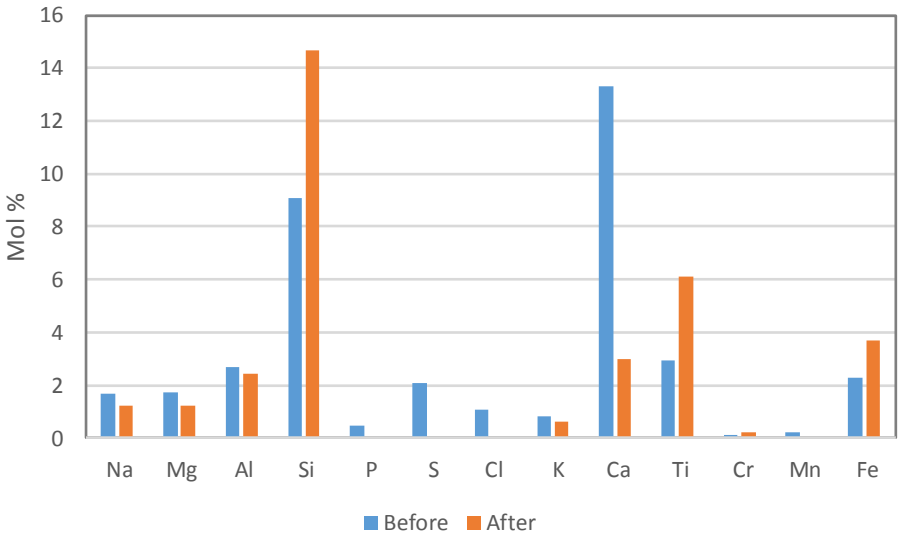


Figure 3. SEM-EDX of T1 ash before and after the leaching procedure.

2.2. Ash T2

The leaching profile for ash T2 is similar to T1. More Sb is leached during the first 30 min. with water. The total percentages of Co, Cu, and Sb leached were: 55, 44, and 74%.

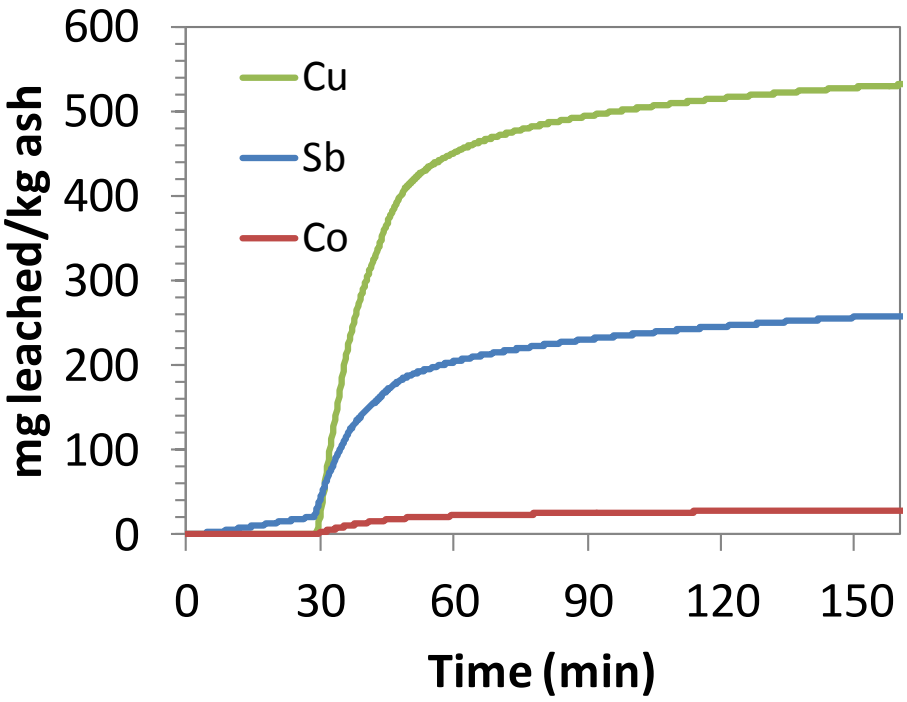
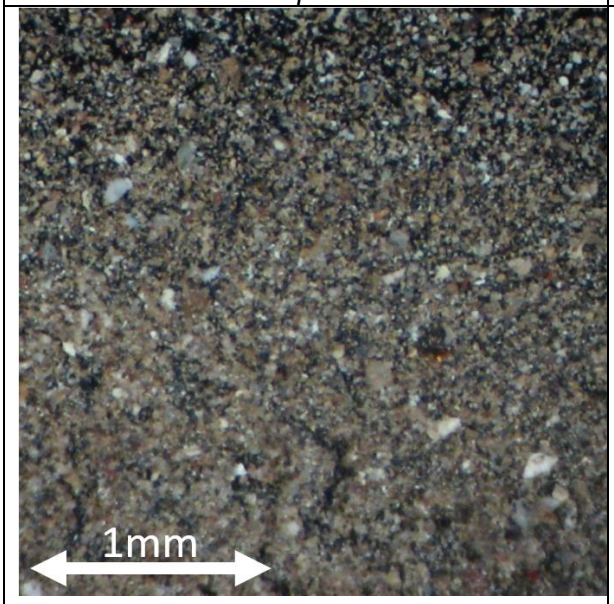
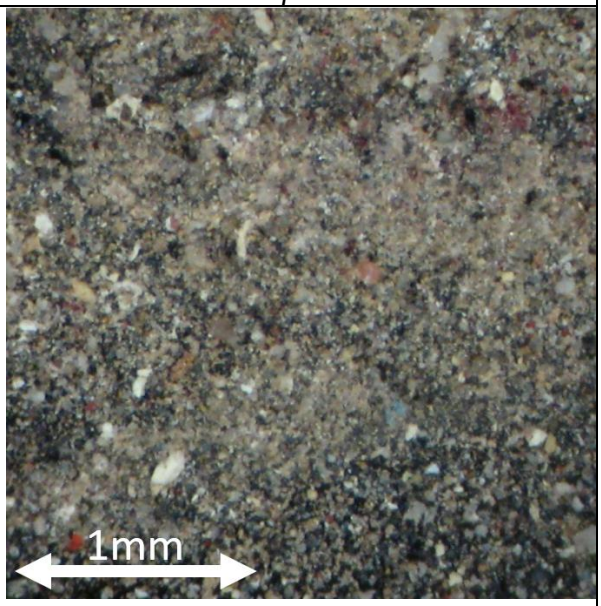
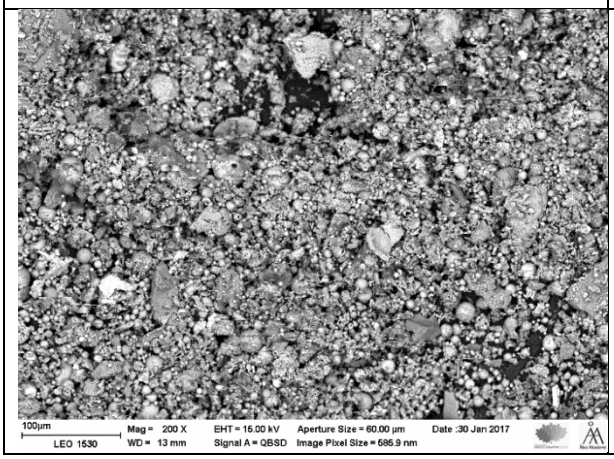
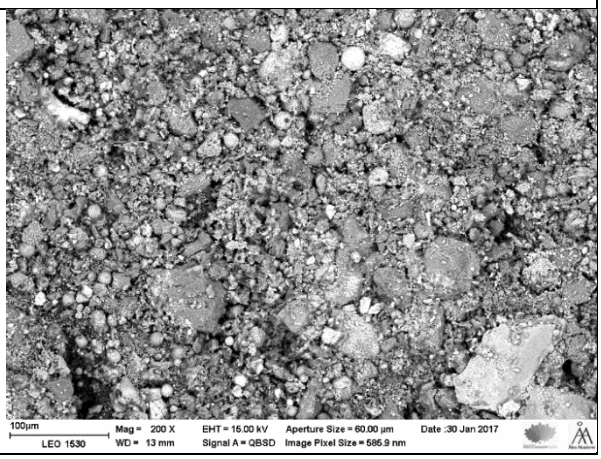


Figure 4. Leaching results of Co, Cu, and Sb of T2 ash. The ash was leached with water for the first 30 min. and then with a 5% HNO_3solution.

Table 4. Microscope and SEM pictures of T2 ash before and after the leaching procedure.

Before	*After*
	
	

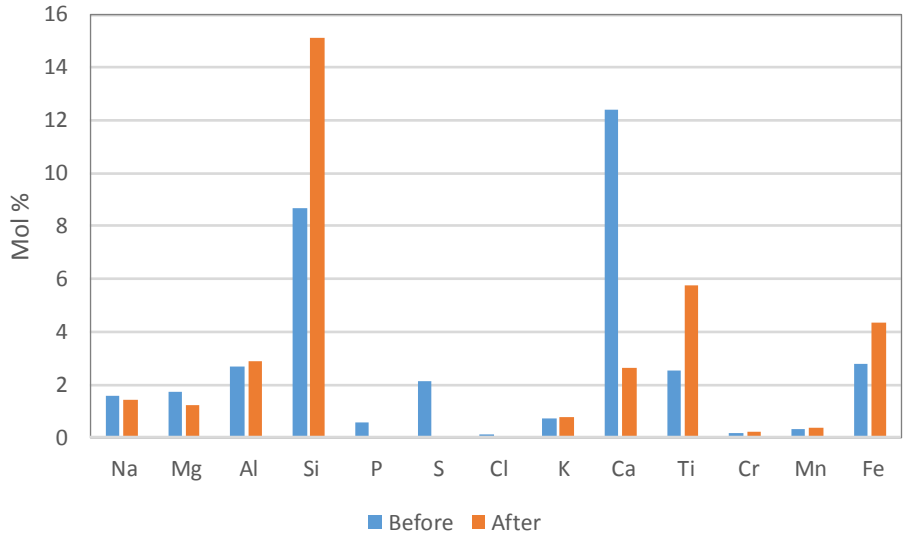


Figure 5. SEM-EDX of T2 ash before and after the leaching procedure.

2.3. Ash T3

The leaching profile for ash T3 is similar to the previous ones. The total percentages of Co, Cu, and Sb leached were: 53, 43, and 59%.

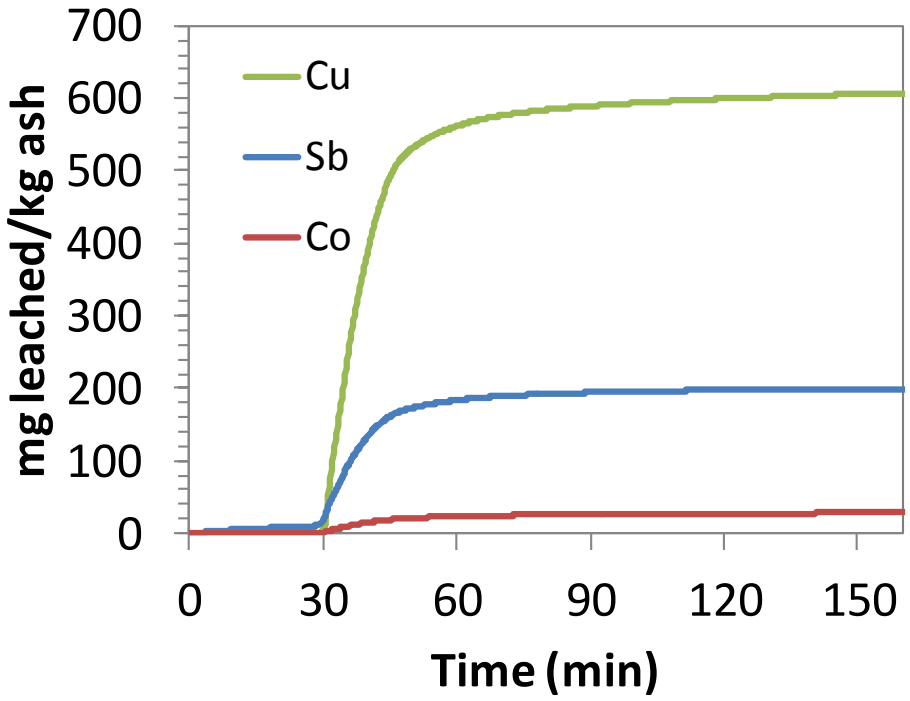
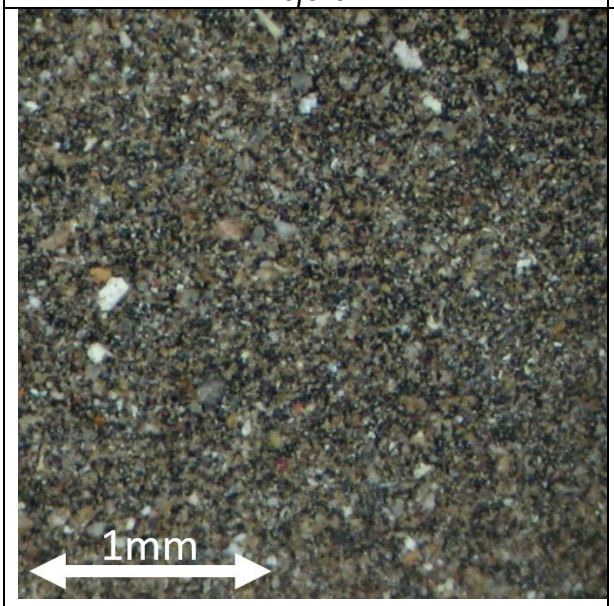
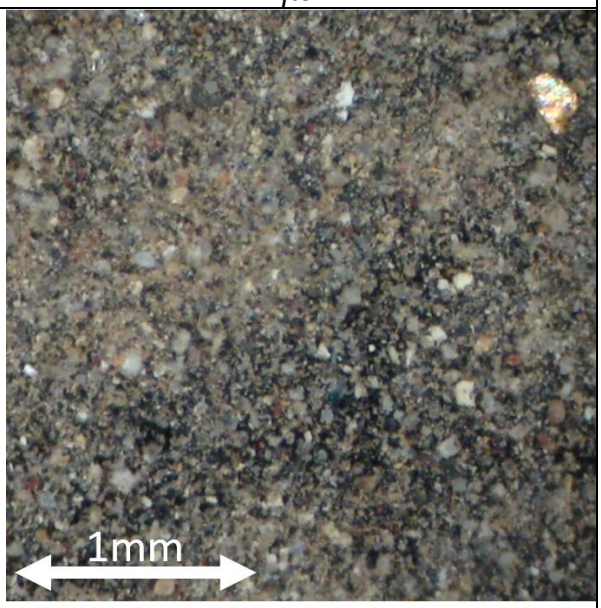
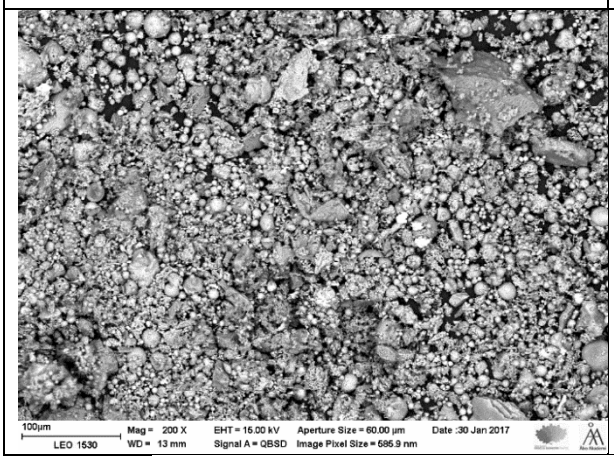
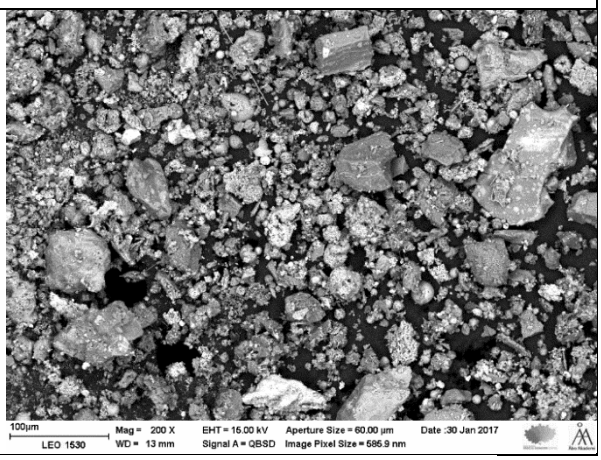


Figure 6. Leaching results of Co, Cu, and Sb of T3 ash. The ash was leached with water for the first 30 min and then with a 5% HNO_3-solution.

Table 5. Microscope and SEM pictures of T3 ash before and after the leaching procedure.

Before	*After*
	
	

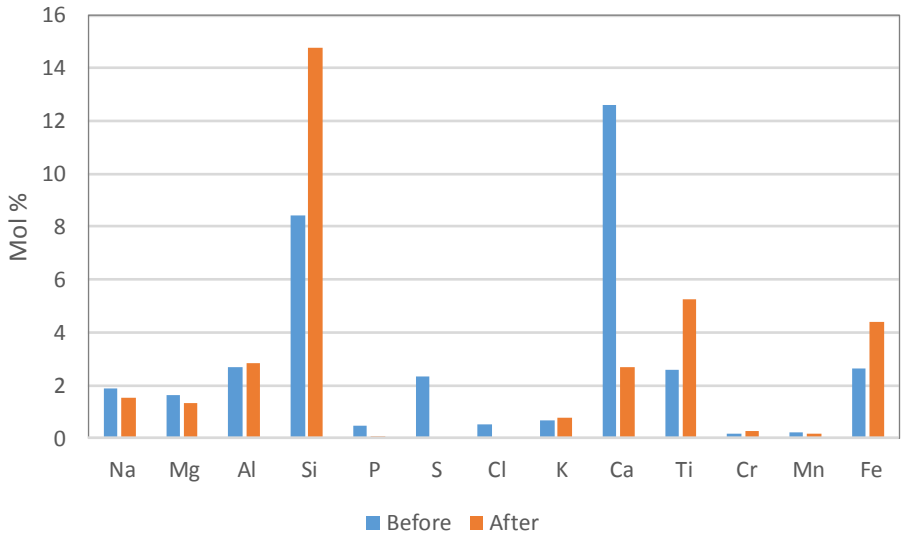


Figure 7. SEM-EDX of T3 ash before and after the leaching procedure.

2.4. Ash T4

The leaching profile for ash T4 is also similar to the previous ones. The total percentages of Co, Cu, and Sb leached were: 56, 52, and 49%.

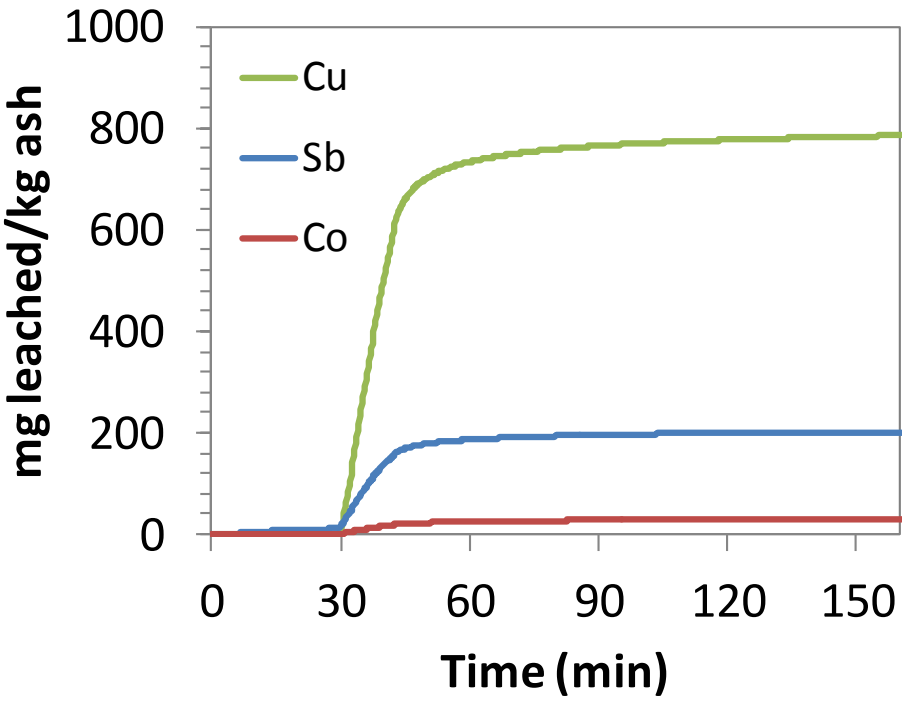
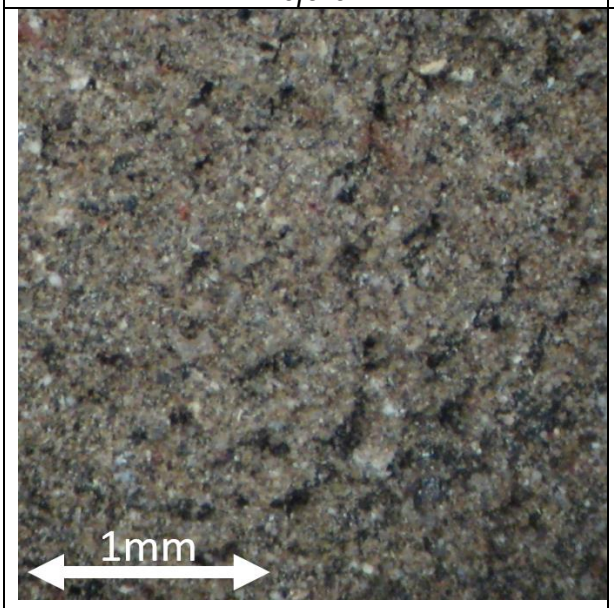
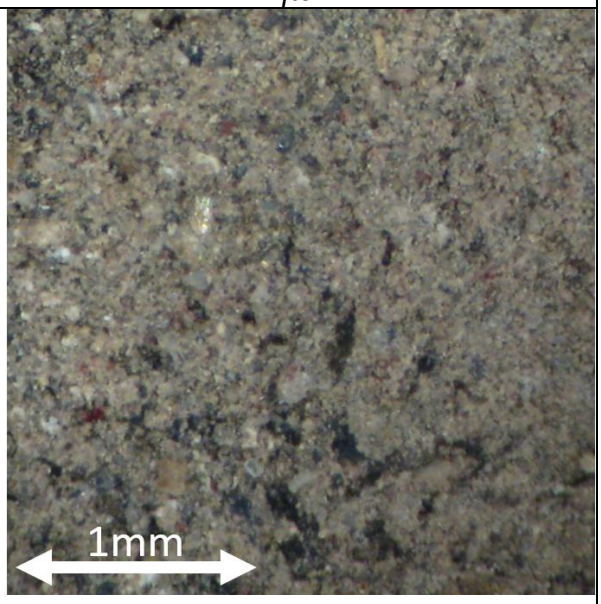
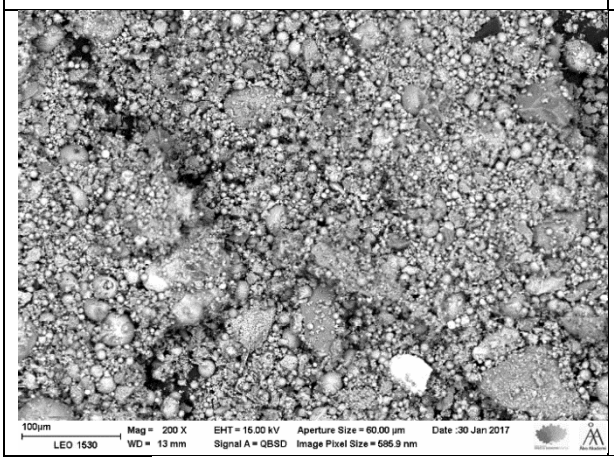
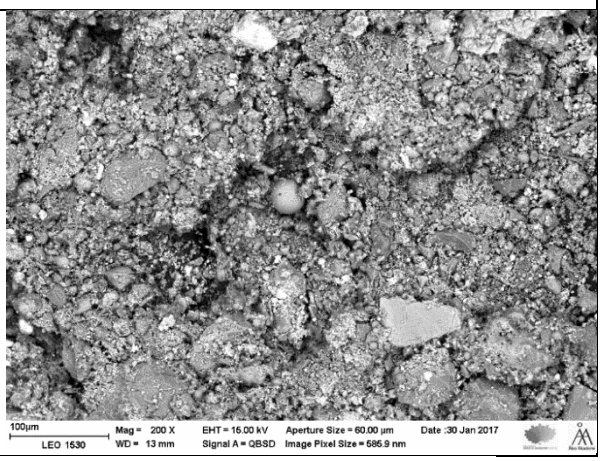


Figure 8. Leaching results of Co, Cu, and Sb of T4 ash. The ash was leached with water for the first 30 min and then with a 5% HNO_3-solution.

Table 6. Microscope and SEM pictures of T4 ash before and after the leaching procedure.

Before	*After*
	
	

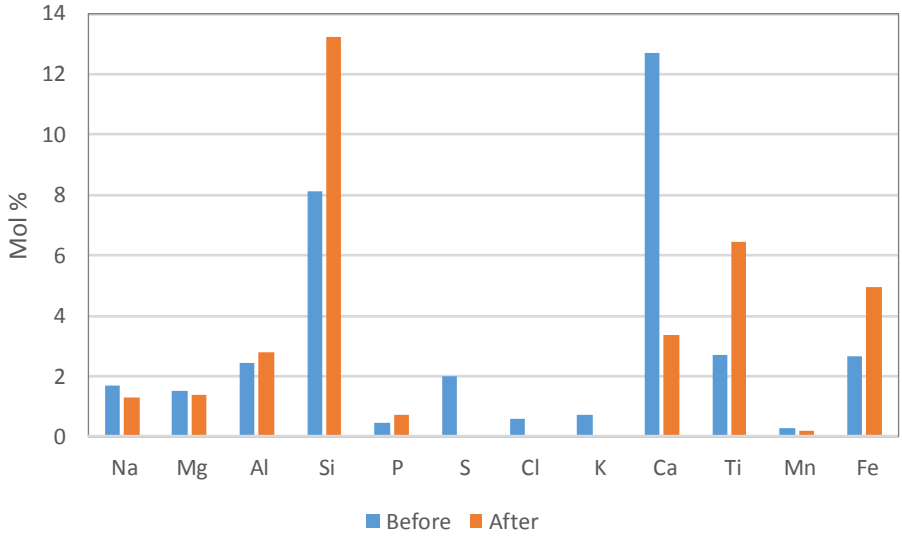


Figure 9. SEM-EDX of T4 ash before and after the leaching procedure.

2.5. Ash T5

The leaching profile for ash T5 is similar to the previous ones. The total percentages of Co, Cu, and Sb leached were: 50, 57, 40%.

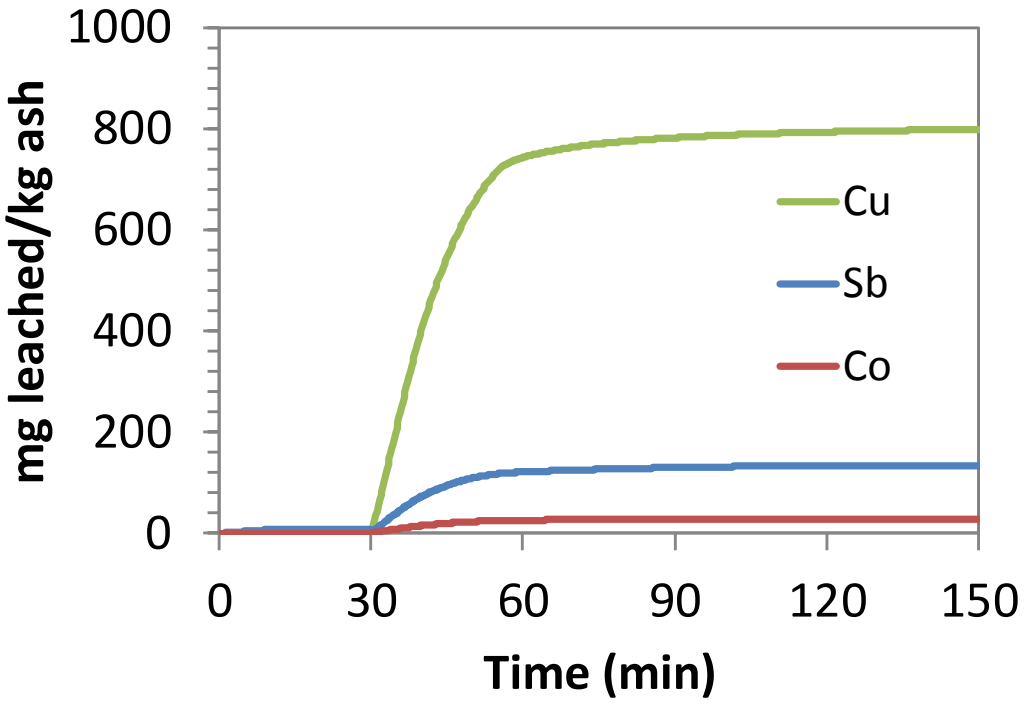
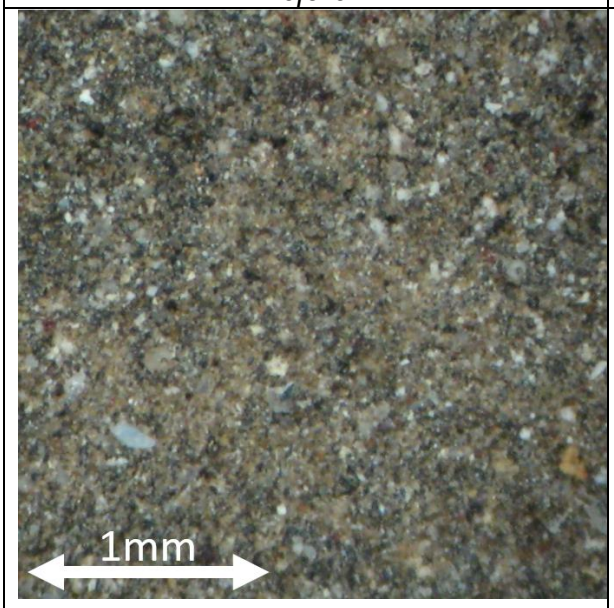
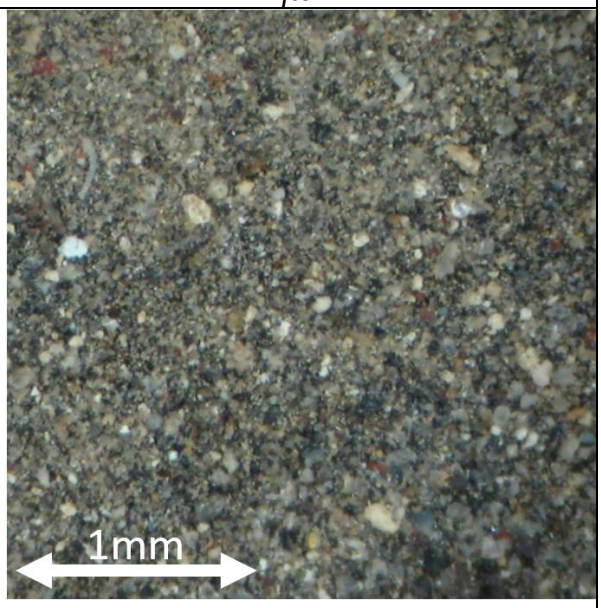
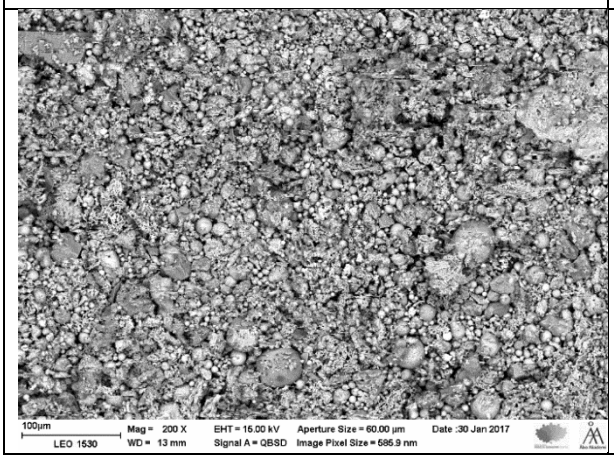
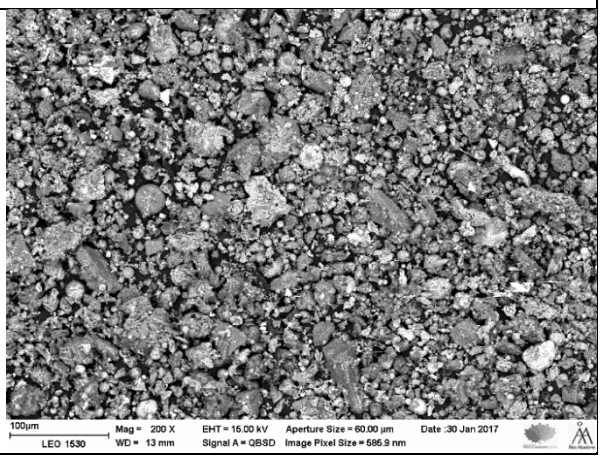


Figure 10. Leaching results of Co, Cu, and Sb of T5 ash. The ash was leached with water for the first 30 min and then with a 5% HNO_3-solution.

Table 7. Microscope and SEM pictures of T5 ash before and after the leaching procedure.

Before	*After*
	
	

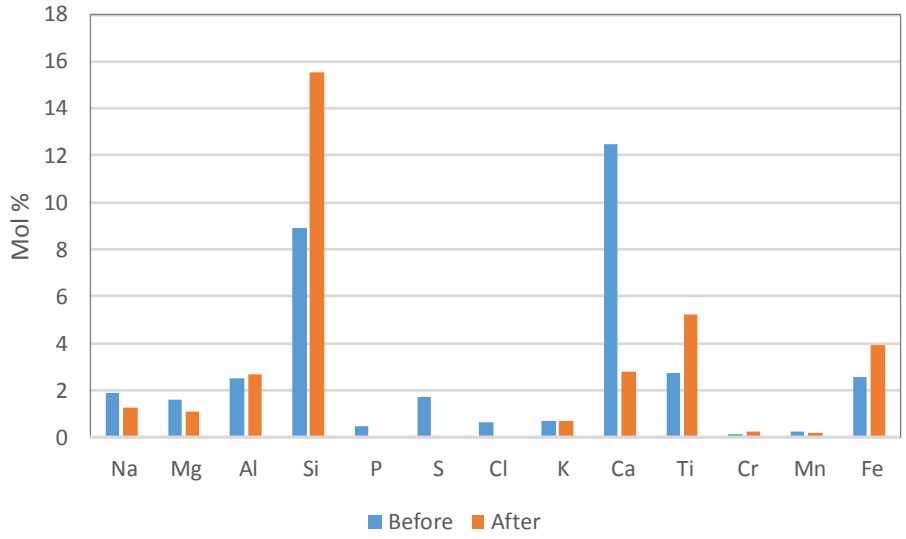


Figure 11. SEM-EDX of T4 ash before and after the leaching procedure.

2.6. Ash T5 with 24h water leaching before HNO_3

One experiment with a longer, 24h, water-leaching step was made. During the 24h leaching the elements were not analyzed continuously. 40% of Sb was leached in the water leaching step, however, no Co or Cu was leached out (Figure 12). Significant amounts of Ca, K, Na, and S were also leached in the water leaching. After the water leaching the ash was leached with 5% HNO_3. The acid leaching seems to be enhanced by the long water leaching step. The leaching of Co, Cu, and Sb is fast (Figure 13), and the total percentages of Co, Cu, and Sb leached were: 67,66, and 79%.

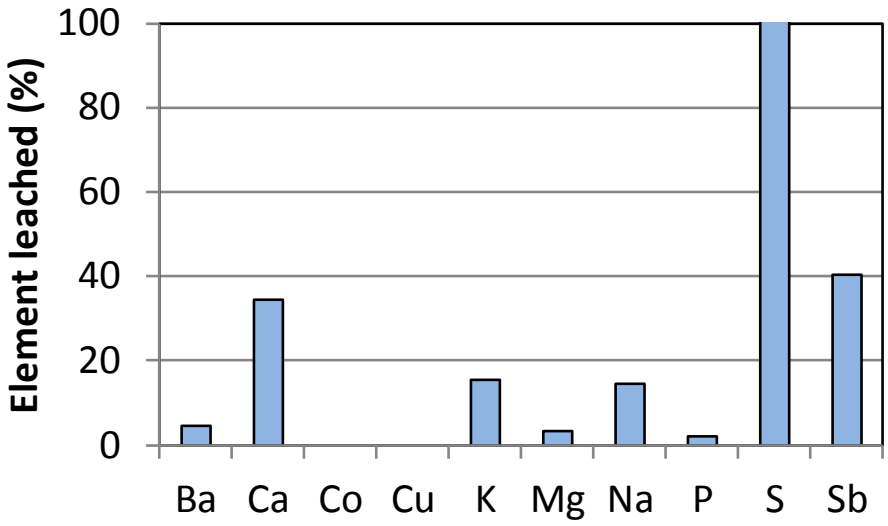


Figure 12. Elements leached during the 24 h water leaching.

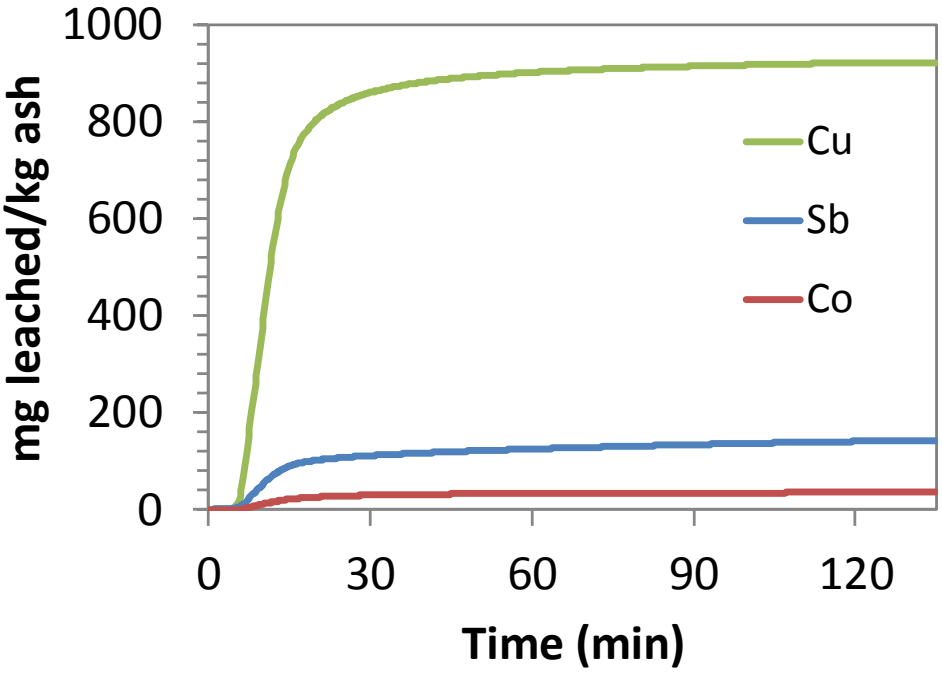
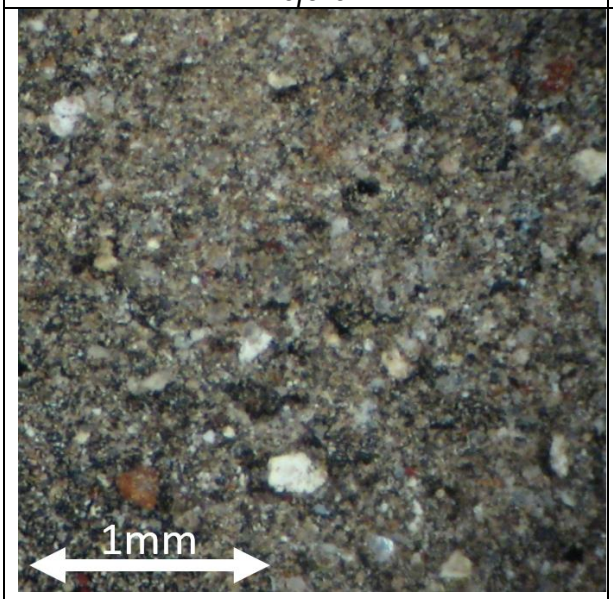
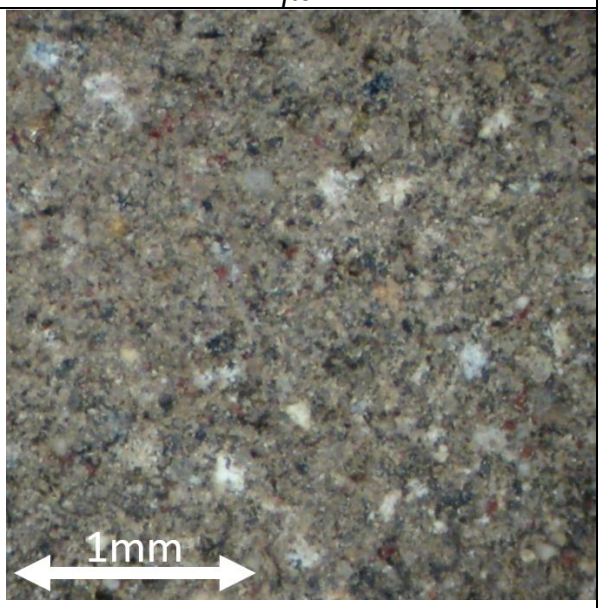
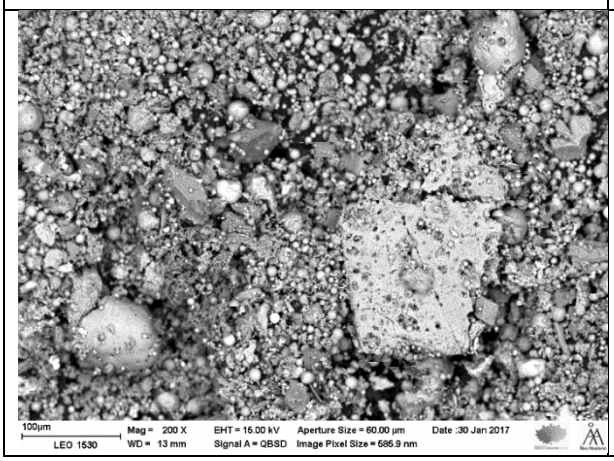
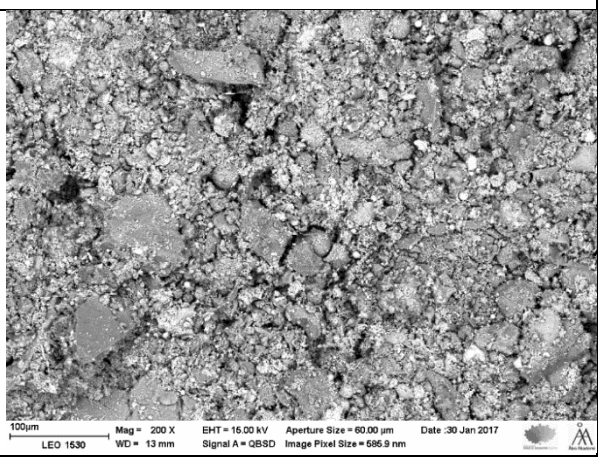


Figure 13. Leaching results with 5% HNO_3-solution of Co, Cu, and Sb of T1 ash. The ash was leached with water for the first 24 h (results in Figure 12) and then with a 5% HNO_3-solution.

Table 8. Microscope and SEM pictures of T5 ash before and after the leaching procedure.

Before	*After*
	
	

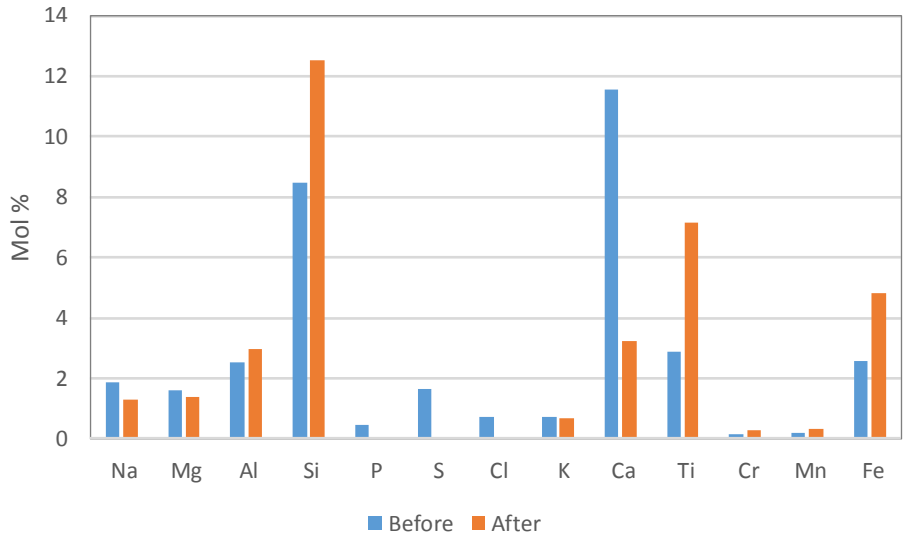


Figure 14. SEM-EDX of T5 ash before and after the leaching procedure.

2.7. *Effect of cyclone temperature on leachability of Cu*

Figure 15 shows the leachabilty of Cu for the different ashes. It seems that Cu is more easily leached for the ashes from the lower cyclone temperature cases.

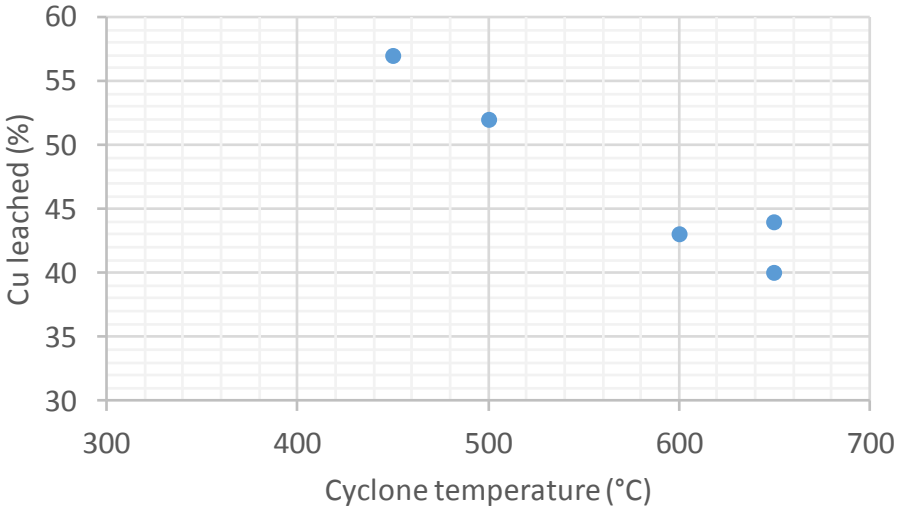


Figure 15. Leaching of Cu as a function of cyclone temperature.

3. Summary and conclusions

A procedure for the continuous analysis of elements leached from fly ashes using different leachates has been developed. This method enables 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 cell, 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 cell can be adjusted. The method enables for rapid testing of different parameters with the on-line analysis of the leached elements. The method can be used to find optimal parameters for leaching various elements.

Five ashes were tested (T1-T5) in the second part of the project. The ashes were from test runs made at the VTT CFB boiler. Ash T1 was from the co-combustion of demolition wood and plastic cables, and ashes T2-T5 were from combustion of demolition wood. The main emphasis was laid on 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 ash 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% HNO_3 was pumped through the ash for 2 h 10 min. Only some Sb was leached during the water leaching step. Co and Cu were leached only when HNO_3 was used as solvent. The leaching rate was faster during the first 15 min with acid. The leaching behaviour was similar for all the ashes (Figure 16). T5 was also tested using a 24 h water leaching step before the acid leaching. 40% of Sb was leached out during this step. The

acid leaching step seemed to be enhanced by the long water leaching step, with higher Co and Cu leached out compared to the normal leaching procedure.

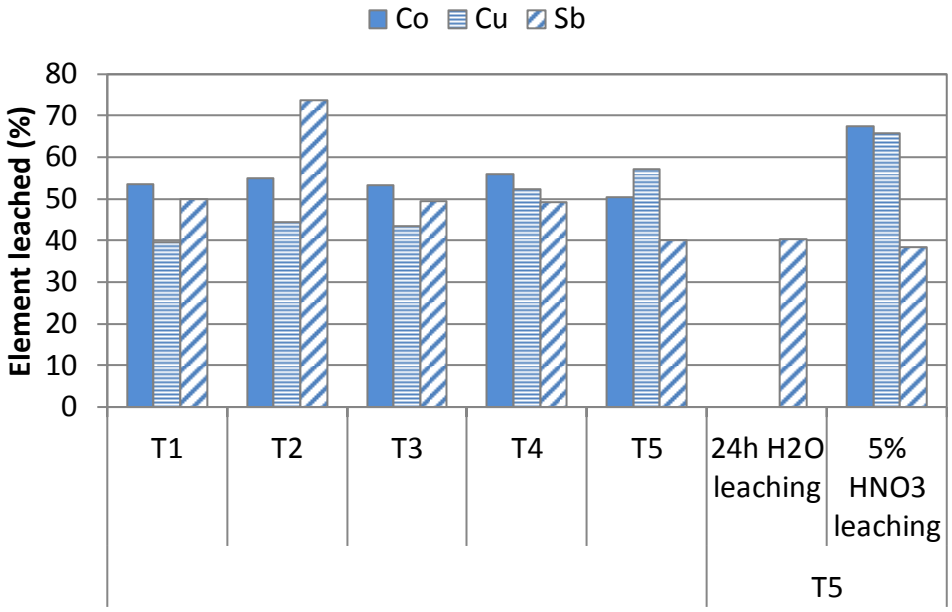


Figure 16. Co, Cu, and Sb leached during the leaching procedure.

4. 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.