## Supplementary Material

**1. Particle size distribution**

**2.Sequential extraction**

**3. Washing experiments on untreated MSWI-FA**

**4. Phase analysis after washing**

## 1.Particle size distribution

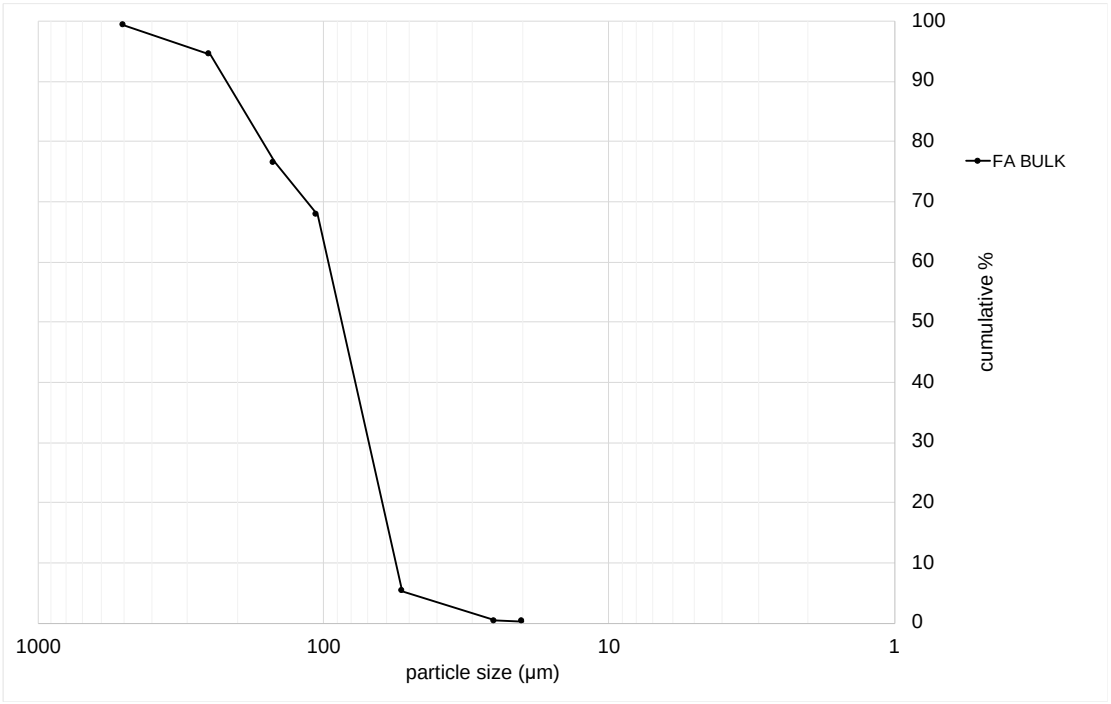



**Figure S1.** Particle size distribution of fly ash. X-axis: particle size (µm), $\log_{10}$-scale; Y-axis: cumulative weight percentage. The reported particle size distribution is the average of measurements on four independent samples; error bars are determined as the related expected standard deviations**.**

## 2.Sequential extraction procedure

*Step 1 (acid-soluble):* an aliquot of 8 ml of magnesium chloride (1 mol/L) was added to 1 g of dry FA in a 100 ml glass container. The mixture was shaken for 16 h (overnight) with a magnetic stirrer at room temperature at a speed of 40 rpm. The extract was separated from the solid residue by filtration through a 0.45 µm cellulose nitrate filter (47mm diameter). The extract was analysed immediately or stored at 4 °C. The solid residue was washed with deionized water and underwent step 2.

*Step 2 (acid-soluble):* an aliquot of 40 ml of acetic acid (0.11 mol/L) was added to the residue obtained in step 1. The mixture was shaken for 16 h (overnight) with a magnetic stirrer at room temperature at a speed of 40 rpm. The extract was separated from the solid residue by filtration through a 0.45 μm cellulose nitrate filter (47mm diameter). The extract was analysed immediately or stored at 4 °C. The solid residue was washed with deionized water and underwent step 3.

*Step 3 (reducing conditions):* in a 100 ml glass container, an aliquot of 40 ml of hydroxylammonium chloride (0.1 mol/L, adjusted to pH 2 with nitric acid) was added to the residue obtained in step 2. The mixture was shaken for 16 h (overnight) with a magnetic stirrer at room temperature at a speed of 40 rpm. The extraction procedure was then performed as described above. After washing with deionized water, the solid residue underwent step 4.

*Step 4 (oxidizing conditions):* an aliquot of 10 ml of hydrogen peroxide (8.8 mol/L) was carefully added in small aliquots to the residue obtained in step 3 in a 100 ml glass container. The container was covered with a watch glass and left at room temperature for 1 h with occasional manual shaking. The procedure was continued for another hour at 85 °C and the volume reduced to a few ml by further heating of the uncovered glass container. A further aliquot of 10 ml of hydrogen peroxide (8.8 mol/L) was added to the residue. The container was covered again and heated at 85 °C for 1 h. The cover was removed and the volume reduced almost to dryness. After cooling, 50 ml of ammonium acetate (1 mol/L adjusted to pH 2 with nitric acid) were added to the residue. The mixture was shaken for 16 h (overnight) with a magnetic stirrer at room temperature at a speed of 40 rpm. The extraction procedure was then continued as described in the previous steps. After washing with deionized water, the solid residue was digested with strong acids (step 5).

*Step 5 (remaining residue)*: a digestion of this fraction has been carried out using the last step of Tessier's procedure. The solid residue was digested with a 5:1 mixture of hydrofluoric and perchloric acids. The solid was first dissolved in a Teflon beaker with a solution of concentrated $HClO_4$ (2 ml) and HF (10 ml) to near dryness. Subsequently, a second aliquot of $HClO_4$ (1 ml) and HF (10 ml) was added, and again the mixture was evaporated to near dryness. Finally, $HClO_4$ (1 ml) alone was added, and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12N HCl and diluted to 25 ml. The resulting solution was then analysed by ICP-MS.

**Table S1**. Sequential extraction method parameters.

| **Steps** | **Reagents and extraction conditions** | **Target phases** |
|---|---|---|
| *Step 1* | 8 ml magnesium chloride (1 M) | Exchangeable |

| | | |
|---|---|---|
| *Step 2* | 40 ml acetic acid (0.11 M), pH 5.5 | acid-soluble (carbonate and salt) |
| *Step 3* | 40 ml hydroxylammonium chloride (0.1 M) and adjusted to pH 2 with 10 M $HNO_3$ | easily reduced (iron oxyhydroxide) |
| *Step 4* | 20 ml hydrogen peroxide (8.8M)<br>50 ml ammonium acetate (1 M) adjusted to pH 2 with 10 M $HNO_3$ | oxidizable (organic matter and sulfide) |
| *Step 5* | 12 ml HF conc. (10 mL) - $HClO_4$ conc. (2 mL) | residual |

## 2.Washing experiments on untreated MSWI-FA

**Table S2**. Concentration of fly ash washing solutions from the Turin plant, compared with the legislation limits: * Decr. Min. Amb. 27/09/2010 about the landfill of waste; ** D. M. 186/2006 on waste reuse. Concentrations expressed in mg/L.

| | **L/S 2** | **L/S 5** | **L/S 10** | **L/S 20** | **L/S 50** | **Inert*** | **Non hazardous*** | **Hazardous** | **Reuse**** |
|---|---|---|---|---|---|---|---|---|---|
| conductivity (μs/cm) | 102000 | 52000 | 32000 | 19000 | 8600 | | | | |
| pH | 12 | 12 | 12 | 12 | 12 | | | | 5.5-12 |
| weight loss % | 5 | 10 | 12 | 18 | 21 | | | | |
| Na (mg/L) | 17424 | 5353.2 | 3138 | 1417.2 | 589.32 | | | | |
| K | 19362 | 6324 | 3195 | 1567.2 | 636.6 | | | | |
| Ca | 1503.6 | 1334.4 | 1263.9 | 832.56 | 345 | | | | |
| Mg | 17.364 | 17.256 | 8.613 | 3.3924 | 1.7004 | | | | |
| Chloride | 43888 | 15763 | 8698 | 5266 | 1217 | 80 | 2500 | 2500 | 100 |
| Bromide | 517 | 225 | 115 | 68 | 19 | | | | |
| Fluoride | 13 | 15 | | 2.2 | | 1 | 15 | 50 | 1.5 |
| Sulfate | 6719 | 3774 | 3085 | 804 | 600 | 100 | 5000 | 5000 | 250 |
| Nitrate | n.d. | n.d. | n.d. | n.d. | n.d. | | | | 50 |
| Cr | 11.772 | 12.87 | 6.081 | 2.5512 | 1.2648 | 0.05 | 1 | 7 | 0.05 |
| Ni | 0.49692 | 1.9068 | 0.3219 | 0.186 | 0.06126 | 0.04 | 1 | 4 | 0.01 |
| Cu | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.2 | 5 | 10 | 0.05 |
| Zn | 7.02 | 7.056 | 3.999 | 2.4276 | 1.7262 | 4 | 5 | 20 | 3 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Cd | 9.198 | 10.374 | 4.65 | 1.926 | 0.9264 | 0.004 | 0.1 | 0.5 | 0.005 |
| Fe | 67.14 | 30 | 22.245 | 13.092 | 8.526 | | | | |
| Ba | 1.8786 | 2.9136 | 1.3797 | 1.2264 | 1.005 | 2 | 10 | 30 | 1 |
| Pb | 1.2918 | 1.2918 | 1.2918 | 3.468 | 1.2858 | 0.05 | 1 | 5 | 0.05 |

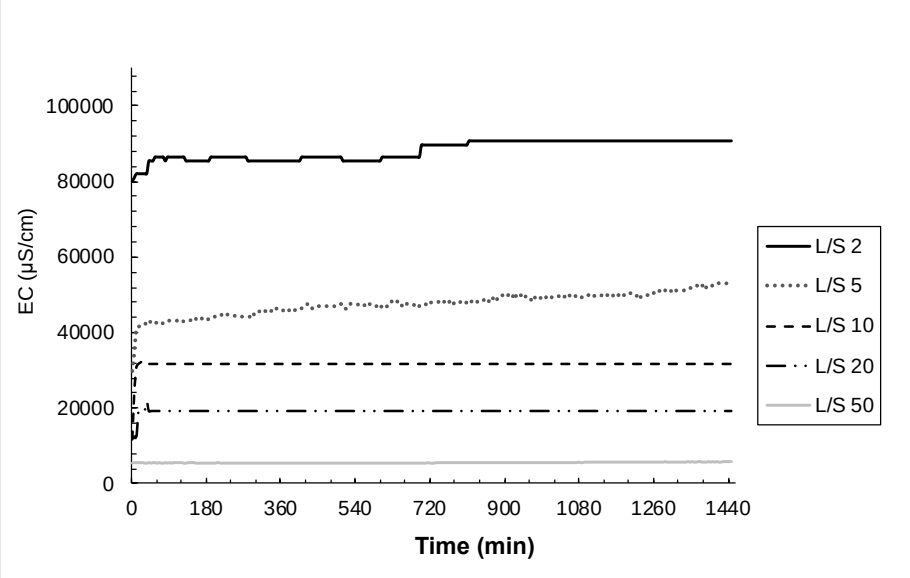



**Figure S3.** Time (min) *versus* EC (µS/cm) of fly ash washing test at different L/S ratios, from 2 to 50.

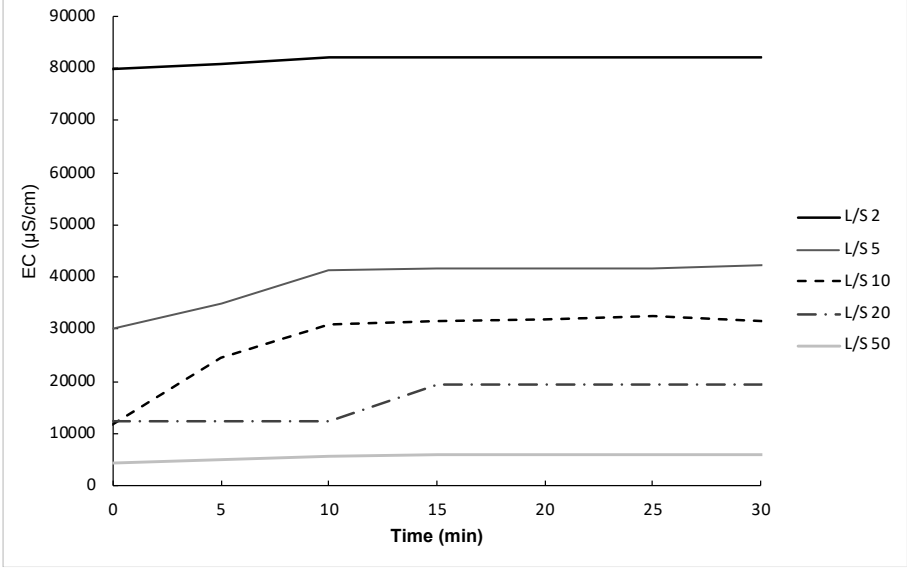



**Figure S4**. Zooming of figure S3 at time 0-30 minutes.

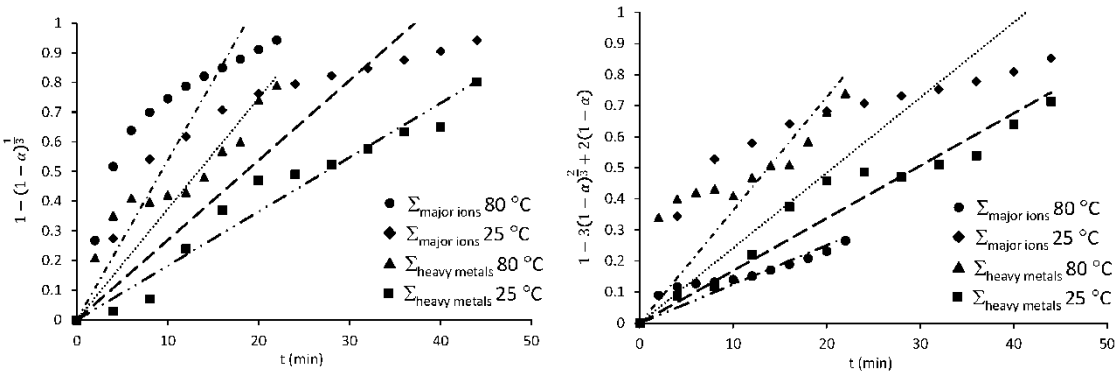



**Figure S5.** SCM plots when chemical reactions (left) or diffusion (right) are considered the rate-determining step.

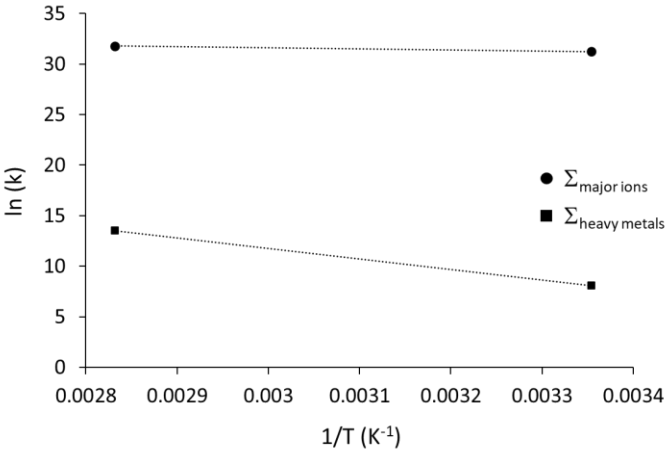



**Figure S6.** Arrhenius plot.