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Waste Wood Fly Ash Treatment in Switzerland: Effects of Co-Processing with Fly Ash from Municipal Solid Waste on Cr(VI) Reduction and Heavy Metal Recovery

Mirjam Wolffers [1,*], **Gisela Weibel** [1,2] and **Urs Eggenberger** [1]

[1] Institute of Geological Sciences, University of Bern, Baltzerstasse 1 + 3, 3012 Bern, Switzerland; gisela.weibel@geo.unibe.ch (G.W.); urs.eggenberger@geo.unibe.ch (U.E.)
[2] Zentrum für nachhaltige Abfall- und Ressourcennutzung ZAR, Wildbachstrasse 2, 8340 Hinwil, Switzerland
* Correspondence: mirjam.wolffers@geo.unibe.ch

Abstract: In Switzerland, waste wood fly ash (WWFA) must be treated before deposition on landfills due to its high pollutant load (Cr(VI) and heavy metals). Acid fly ash leaching, the process used for heavy metal recovery from municipal solid waste incineration fly ash (MSWIFA), represents a possible treatment for heavy metal depletion and Cr(VI) reduction in WWFA. The co-processing of WWFA with MSWIFA during acid fly ash leaching was investigated in laboratory- and industrial-scale experiments with different setups. Of interest were the effects on heavy metal recovery efficiency, the successful outcome of Cr(VI) reduction and consumption of neutralizing chemicals (HCl, H_2O_2). Detailed chemical and mineralogical characterization of two WWFA types and MSWIFA showed that MSWIFA has higher concentrations in potentially harmful elements than WWFA. However, both WWFA types showed high concentrations in Pb and Cr(VI), and therefore need treatment prior to deposition. Depending on the waste wood proportion and quality, WWFA showed chemical and mineralogical differences that affect leaching behavior. In all experimental setups, successful Cr(VI) reduction was achieved. However, WWFA showed higher consumption of HCl and H_2O_2, the latter resulting in a particularly negative effect on the recovery of Pb and Cu. Thus, co-processing of smaller WWFA portions could be expedient in order to diminish the negative effects of Pb and Cu recovery.

Keywords: wood ash treatment; MSWI fly ash; heavy metal recovery; acid leaching; chromate reduction; hot alkaline extraction

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1. Introduction

The demand for renewable heat and energy production using the CO_2 neutral energy source wood has been growing enormously in Switzerland over the last decades—leading to strongly increasing amounts of wood ashes. In Switzerland, an annual load of 60,000 t wood ash arises from automatic firings through the energetic use of natural wood (e.g., forest) and from the thermal utilization of waste wood (e.g., coated, painted wood) [1]. A quarter thereof represents wood ash from waste wood enriched in heavy metals and Cr(VI). Depending on the incinerator plant and furnace, wood ash can be divided into up to three different fractions: grate ash, cyclone ash and filter ash [2]. The coarse-grained grate ash arises directly from the grate and is equivalent to bottom ash residing from municipal solid waste incineration (MSWI). This is the biggest fraction with roughly 60–90 wt % of the thermal residue [2]. The cyclone ash and the filter ash arise at the flue gas cleaning system and are often collected together and referred to as wood fly ash. Compared to grate ash, wood fly ash is enriched in volatile elements (e.g., Cl, heavy metals) since their low boiling point makes them evaporate during combustion and later precipitate at the flue gas cleaning system [3]. The chemical composition of wood ash is mainly dependent on wood quality and incineration conditions [3,4]. Factors affecting wood quality are wood type, compartment, growing environment and possible treatments (e.g., impregnation) prior to combustion [3,5]. While wood ash from natural wood may be enriched in organic pollutants (e.g., PAH, PCDD-/F [6]) and can contain naturally incorporated heavy metals in elevated concentrations, the contaminated waste wood ash is mostly characterized by highly elevated heavy metal concentrations (e.g., Zn, Pb, Cu, Cr) remaining from paints, coatings or impregnation [7]. Due to the oxidative conditions during combustion, Cr(III) compounds are mainly oxidized to very toxic and highly mobile Cr(VI) [8]. Thermal residues from waste wood which have been impregnated with Cr-bearing compounds are often severely enriched in Cr(VI). In water extraction tests, studies report Cr(VI) concentrations in waste wood ash that exceed the threshold value for landfilling [8,9].

Because of the possibly high contaminant load, wood ash is considered as waste and must be dumped on landfills, although opportunities for recycling are being sought (e.g., in concrete production [10]). The less polluted grate ash and fly ash from natural wood can be deposited without further treatment on landfill type D and E, according to the Swiss Waste Ordinance [11]. Waste wood fly ash (WWFA), however, must be treated before deposition due to the elevated concentrations in Cr(VI) and possibly environmentally harmful heavy metals. As there is currently not enough capacity available in Cr(VI) reducing facilities in Switzerland to treat the entire quantity of WWFA before landfilling, waste wood fly ashes can be deposited temporarily without a prior treatment on landfill type D or E (depending on their total organic carbon (TOC) content (<2 or <5 wt %, respectively) until 2023. From 2023 on, WWFA must be treated in order to reduce Cr(VI) and recover the heavy metals. Acid fly ash leaching with the FLUWA process [12,13] represents a promising method for treating WWFA prior to deposition. The FLUWA process represents the state-of-the-art process in Switzerland for recovering heavy metals (mainly Zn, Cd, Pb, Cu) from the similarly generated MSWI fly ash (MSWIFA). The ash is thereby leached with acid scrub water, acid from the flue gas cleaning system (~5% HCl). Filtration of the ash slurry yields a heavy metal enriched leachate that is then precipitated to a hydroxide sludge for subsequent heavy metal recovery and a filter cake depleted in heavy metals that is deposited on landfills. Because WWFA can yield heavy metal concentrations in the same range as MSWIFA, but occur in smaller quantities, a cotreatment of both ashes could be expedient. Beginning 2021, all Swiss MSWIFA must be treated before deposition [11] and depending on the heavy metal recovery guideline in revision, the use of an oxidant (e.g., hydrogen peroxide (H_2O_2)) will be necessary during the FLUWA process. Oxidizing conditions during metal extraction are a prerequisite to suppress the reductive precipitation of the redox-sensitive elements Cu, Pb, and to a minor extent, Cd. The co-processing of WWFA in the FLUWA process is already carried out at this study's investigation site Energiezentrale Bern, where it is economically favorable to co-process the arising WWFA40, a WWFA with 40% waste wood content. However, the heavy metal extraction efficiency of cotreating WWFA40 and the completeness of Cr(VI) reduction during the FLUWA process have not been investigated in detail.

The aim of the study was, therefore, to investigate the heavy metal recovery, as well as the Cr(VI) reduction efficiency of the FLUWA process when WWFA40 is co-processed. The actual state was investigated (reducing conditions) as well as the future state (oxidizing conditions) when oxidizing conditions become state-of-the-art for the FLUWA process. The industrial process was first simulated in laboratory-scale experiments in order to evaluate the leaching behavior of the different ash types (MSWIFA, WWFA40 and MFA (a mix of the two ashes to simulate the co-processing)) and to quantify the leaching efficiency in terms of heavy metal recovery and amount of neutralizing chemicals. The same experimental setups were later implemented at an industrial scale. Of special interest of the experiments was the heavy metal recovery efficiency, successful outcome of Cr(VI) reduction under reducing and oxidizing processing conditions and consumption of neutralizing chemicals (HCl, H_2O_2). The ashes used in the experiment were characterized with respect to their chemical and mineralogical composition, and their acid-neutralizing capacity (ANC) was determined. For comparison, the sample WWFA100 with 100% waste wood content was analyzed. To assess both the hazard potential of WWFA and the completeness of Cr(VI) reduction, the water-soluble and total content of Cr(VI) were determined for WWFA and filter cakes.

2. Materials and Methods

2.1. Sample Origin, Sampling and Sample Preparation

MSWIFA and WWFA40 samples were collected in 2017 at the waste and wood power plant Energiezentrale Bern. An annual amount of 135,000 t municipal solid waste and 65,000 t of wood (25% water content, fluidized-bed combustion) was incinerated in separate incinerators in 2017. MSW and wood are combusted separately but treated together prior to landfilling with the FLUWA process in two consecutive extraction reactors (1 m^3 each). The co-processing of WWFA40 in the FLUWA is economically favorable since excess acidity of their scrub water is consumed by the alkalinity of the WWFA40, and the use of lime milk is minimized. At present, the FLUWA process at the incineration plant is performed under reducing conditions (without the addition of H_2O_2) with MSWIFA and WWFA40 proportions in the ratio as they are produced. Adjustments of the ash ratio are made in the current process such that a favorable extraction pH of 3.8 is achieved. To perform industrial experiments at oxidizing conditions, a pumping system was installed for continuous dosing of H_2O_2.

In order to understand the geochemical differences between MSWIFA and WWFA40, three representative composite samples of each ash type were investigated in terms of chemical and mineralogical composition. The sampling duration varied between one and three weeks. Samples were taken twice a day and mixed into composite samples. Additionally, three samples of WWFA40 (weekly composite samples) and their corresponding filter cakes were made available for Cr(VI) analyses. For comparison, the sample WWFA100 (100% waste wood, monthly composite sample) from a Swiss biomass power plant was investigated.

Approximately 10 kg of ash was collected in each sampling campaign. The ashes were homogenized and split into 1 kg working batches and dried at 105 °C until constant weight for chemical analysis and at 40 °C for mineralogical analysis.

2.2. Chemical Analysis

The elemental composition of the ashes was obtained through energy-dispersive X-ray fluorescence (ED-XRF) analysis performed on pressed powder pellets (4.0 g ash, 0.9 g wax as a binder) using a Spectron Xepos (SPECTRO, Kleve, Germany) spectrometer with matrix adjusted calibration. For quality control, the samples were analyzed in duplicates. The accuracy of the method was previously verified by the authors [14] through multiple determinations of similar ash samples and the analysis of the standard reference material BCR 176R [15]. The ED-XRF measurements showed good reproducibility within <2% for the elements Cu, Zn, Cd, Sb, Pb, Br, Sn, Ba, within 5% for Al, Si, S, Cl, Ca, Ti, Mn, Fe, Cr, Sr and within <10% for K, Na, Mg. Extract solutions were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Thermo Scientific iCAP 700 Series (Waltham, MA, USA) after dilution with HNO_3 1% and calibrated with the multielement standards CertiPUR IV and X (Merck, Kenilworth, NJ, USA). The analytical error accounts for ±5% for all elements except Na, K, Ca, Sb and S that showed ±10% error based on multiple measurements of certified standard solutions.

2.3. Mineralogical Analysis

The mineralogical composition was obtained throughout X-ray powder diffraction (XRD) analysis using a Panalytical X'Pert Pro diffractometer (CuKα-radiation) (Malvern Panalytical, Almelo, Netherlands). 4 g of material was mixed with 1 g of internal standard (corundum) and ground dry for 6 min at 55 Hz in an XRD McCrone mill from Retsch (Haan, Germany). Measurement was performed on disoriented samples from 5 to 75° 2Theta at 40 kV acceleration voltage and at an electron generating current of 40 mA. An automatic divergence slit was used. For quantification, TOPAS-Academic software (V6, Coelho Software, Brisbane, Australia) was used (Rietveld refinement). The extended uncertainty is attributed to 50% for concentrations <1%, 20% for concentrations <5% and 10% to concentrations >5%. The structural data (*.cif files) of the inorganic crystal structure database (ICSD) was used, and phase concentrations and amorphous part were calculated based on the internal standard.

2.4. Acid-Neutralizing Capacity

Acid-neutralizing capacity (ANC) titration was performed using a 785 DPM Titrino device from Metrohm (Herisau, Switzerland). with 2 g of ash 20 mL ultrapure water. Every 10 min, 1 mL of HCl 1 M was added under continuous stirring until the ash slurry reached a pH of 2.

2.5. Water-Extractable Cr(VI)

The content of water-soluble Cr(VI) was determined in WWFA samples in order to make statements about the hazard potential of WWFA. Furthermore, the content of water-soluble Cr(VI) in the filter cakes was determined to examine the completeness of the Cr(VI) reduction during the FLUWA process. Cr(VI) analyses were performed on the eluates obtained with the standard eluate test F-22 [16]. The ash and filter cake samples were thereby eluted with ultrapure water for 24 h at a liquid to solid (L/S) ratio of 10 (4 g ash, 40 mL ultrapure water). For quality control, as well as to investigate transformations in the redox state during the eluate test, Cr(III) and Cr(VI) spikes were added, and the eluate test was performed two times per sample, each spiked and unspiked. Selected samples were further eluted as duplicates. For the spiking, the concentration of 50 mg/kg Cr(III) in the form of $CrNO_3 \cdot 9H_2O$ and 10 mg/L CrO_4^{2-} for the Cr(VI) spike were added for the eluate test. The comparison of the Cr(VI) concentrations of the two eluates per sample allowed calculating the recovery of the spike. The water-extractable Cr(VI) content in the eluates was determined spectrophotometrically with a Merck Spectroquant Pharo 100 after complexation with diphenylcarbazide (DPC) at an absorption maximum of 540 nm. For complexation, a Spectroquant chromate test set (Merck, No 1.14758, Darmstadt, Germany) was used. No determination of Cr(VI) in the FLUWA leachate was performed as the Cr concentration in the leachates were below the detection limit in all samples.

2.6. Total Cr(VI)

For a more comprehensive assessment of the hazard potential of Cr(VI), the total content of Cr(VI) was determined for two WWFA samples (WWFA40_2 and WWFA100). Total Cr(VI) extraction on WWFA was performed on duplicates by hot alkaline extraction (method 3060A [17]). For quality control, the standard reference material NIST 2701 [18] was analyzed for total Cr(VI) content, and the determined value was within the given uncertainty. The accuracy of the method on similar materials was previously verified [19] by the authors, and reproducibility within 10% was attributed to the method based on spike recoveries and multiple measurements of the standard reference material [20]. Analysis of Cr(VI) concentration in the extract solutions was performed with ICP-OES after the use of CHROMAFIX PS-H+ cation exchange cartridges (Macherey–Nagel, Düren, Germany) in order to retain Cr(III). The effectiveness of the cartridges on similar extract solutions was tested in previous studies [19]. In order to investigate Cr redox transitions during extraction, a parallel extraction with Cr(VI) spiking was performed for each sample by adding a concentration of 100 mg/kg $PbCrO_4$.

2.7. Laboratory Experiments

In order to investigate the effects of co-processing WWFA40 in the FLUWA process, the process was simulated on a laboratory-scale at conditions feasible on an industrial-scale. At a laboratory-scale, mass balances can be quantified precisely, and process conditions (pH, Eh) can more easily be controlled. Three different ash types were used for the experiment:

MSWIFA (sample MSWIFA_2), WWFA40 (sample WWFA40_2) and MFA (the ash mix of WWFA40_2 and MSWIFA_2, mixed at a ratio of 1:2, to simulate a cotreatment). Two different experimental setups were performed at a laboratory-scale (Table 1): without the use of H_2O_2 (30%) and with a concentration of 40 L H_2O_2/t ash, which represents standard plant conditions. All experiments were performed two times in order to assure reproducibility.

Table 1. Experimental setups for laboratory- and industrial-scale experiments.

		Laboratory-Scale			**Industrial-Scale**		
	Ash Type	**MSWIFA**	**MFA**	**WWFA40**	**MSWIFA**	**MFA**	**WWFA40**
Without H_2O_2	Extraction pH	3.8	3.8	3.8	3.7–4.1	3.8–4.2	3.7–4.3
	Leachate pH	4.8	4.8	5.4	3.8–4.4	4.0–4.5	4.2–4.8
	Experiment duration (h)	1	1	1	8	4	5
40 L H_2O_2/t ash	Extraction pH	2.5	2.5	2.5	3.3–3.8	3.5–4.2	-
	Leachate pH	4.5	4.5	4.2	3.9–4.4	3.8–4.4	-
	Experiment duration (h)	1	1	1	21	18	-
60 L H_2O_2/t ash	Extraction pH	-	-	-	3.5–3.8	3.7–4.3	-
	Leachate pH	-	-	-	3.8–4.3	3.8–4.5	-
	Experiment duration (h)	-	-	-	24	6	-

150 mL of artificial acid scrub water (HCl 5% with 25 g/L $NaSO_4$) was heated in a beaker glass to 40 °C before adding the ash (50 g, liquid to solid ratio L/S = 3). Due to the exothermic reaction between the scrub water and the ash, the temperature rose immediately to 60 °C. Under continuous stirring, the ash slurry reacted for 60 min at 55–60 °C. The pH and Eh values (Ag/AgCl) were recorded temperature-compensated. The pH was controlled by adding HCl (32%). Before filtration, the pH was adjusted to a value of 3.8 with NaOH (65%). The slurry was filtered with a vacuum filter device. 100 mL of deionized water was used to wash the filter cake. For the experiments performed with H_2O_2, a concentration of 40 L/t H_2O_2 was added by 10 consecutive portions (at a 3 min interval) to the ash slurry in the first half of the experiment. The leachates were diluted with HNO_3 1% and further analyzed by ICP-OES. The filter cake was weighed and dried at 105 °C until a constant mass was reached. The heavy metal recovery was determined from mass balance calculations.

2.8. Industrial-Scale Experiments

Both the current state (reducing conditions) as well as the future state (oxidizing conditions) were investigated at an industrial scale (Table 1). Each ash type (MSWIFA, WWFA40 and MFA (ratio WWFA40 to MSWIFA of 1:2.5)) was treated separately without the addition of H_2O_2. Additionally, experiments with 40 and 60 L/t H_2O_2 (30%) (Merck, Darmstadt, Germany) were performed for MSWIFA and MFA. At laboratory-scale experiments, it was shown that WWFA40 required higher H_2O_2 dosages for oxidizing conditions to persist. Therefore, industrial-scale experiments were also conducted with 60 L/t. The efficiency of the cotreatment of WWFA40 and MSWIFA was compared to the scenarios where only WWFA40 or MSWIFA was treated solely. It was found that the treatment of wood ash solely is difficult at an industrial scale due to difficulties with filtration. Therefore, the industrial-experiments with WWFA40 solely were not carried out with H_2O_2 and the focus was put on the cotreatment with MSWIFA.

The different experimental setups were performed at Energiezentrale Bern on different days for time periods between 4 and 24 h. A calculated amount of H_2O_2 was added continuously to the first extraction reactor. During each experiment, multiple samples (in 30- or 60-min intervals, depending on the experiment duration) were taken from the input ash and from the filter cake and combined into composite samples. The pH and Eh were monitored. An average L/S-ratio of 15 was calculated on annual mass flux balances since flow measurement of the leachate is not implemented. The ash and filter cake samples were dried at 105 °C and analyzed for their elemental composition with ED-XRF in order to calculate the recovery.

3. Results

3.1. Chemical Composition

The main constituents of MSWIFA are Ca, Cl, Si, S, Na (>75,000 mg/kg, Table 2). Zn, K, Al (>35,000 mg/kg) and Fe (>10,000 mg/kg) are subsidiary constituents. WWFA differ in chemical composition from MSWIFA, and there are also chemical differences between WWFA40 and WWFA100. WWFA generally shows higher Ca and Si concentrations (>100,000 mg/kg) than MSWIFA, followed by K, Al, Cl, S, Fe (>20,000 mg/kg). Notable is the higher concentration in S and heavy metals (mainly Pb, Zn, Cu) in WWFA100 compared to WWFA40, the latter showing higher concentrations in matrix elements (Ca, Si, K, Mg) in contrast. The concentrations of the main- and subsidiary constituents in the three MSWIFA samples vary within 10–20%, but Cu shows variations by more than 30%. The variations in chemical composition are smaller for WWFA40 than for MSWIFA. The element concentrations vary mostly within 10% between the three WWFA40 samples (except for about 20% for Cr, Mn and Pb). MSWIFA shows strongly elevated concentrations in the potentially harmful heavy metals Pb, Cu, Sb, Cd, some exceeding the threshold for landfilling by multiple times (Pb) or orders of magnitude (Sb, Cd). WWFA shows considerably lower Cd and Sb concentrations (lower by almost two and three orders of magnitude, respectively) but shows strongly elevated Pb concentrations. In two samples of WWFA40, Pb concentration is only 10% lower than in MSWIFA. In WWFA100, Pb concentrations exceed those in MSWIFA by more than double. Zn and Cu concentrations in WWFA40 are about one-third of the concentration in MSWIFA, and in WWFA100, about half. In contrast, WWFA shows higher concentrations in Ba, Cr, Fe, Mn and Ti concentrations than MSWIFA. WWFA100 further shows a very high TOC content of 74,400 mg/kg—which exceeds the threshold value for landfilling.

3.2. Mineralogical Composition

The difference in chemical composition between MSWIFA and WWFA is also represented by a different mineralogical composition (Table 3). As a result of the high Cl content, Cl salts such as halite, sylvite and the Zn bearing K_2ZnCl_4 are important phases in MSWIFA. Anhydrite represents another main phase, together with several silicates (e.g., gehlenite) and calcite. The main mineralogical differences between WWFA40 and WWFA100 are in calcite and anhydrite content. WWFA40 show very high calcite concentrations (17–28 wt %) and high concentration in quartz (7–10 wt %). Sylvite, periclase and Ca-, Al-, Na- silicates form minor components in WWFA40. WWFA100 shows calcite, gehlenite, anhydrite and magnesite as main phases (>7 wt %), followed by minor concentrations in quartz and Ca-, Al-, Na- silicates. The presence of amorphous phases is clearly visible in all spectra by a bump in the background between 20 and 40° 2Theta and was calculated to make 35–50% of the total content.

Table 2. Elemental composition of the analyzed municipal solid waste fly ash (MSWIFA) and waste wood fly ash types WWFA40 and WWFA100, determined by energy-dispersive X-ray fluorescence (ED-XRF).

		MSWIFA			**WWFA40**		**WWFA100**
		mg/kg			**mg/kg**		**mg/kg**
	MSWIFA_1	**MSWIFA_2**	**MSWIFA_3**	**WWFA40_1**	**WWFA40_2**	**WWFA40_3**	**WWFA100**
Al	39,315	45,558	37,210	46,912	44,985	42,520	32,200
Ba	1928	1996	1679	5091	4681	5107	5370
Ca	165,984	170,617	163,200	288,884	285,400	307,600	235,650
Cd	277	248	311	26	23	28	71
Cl	82,120	85,100	114,500	31,140	32,800	32,530	36,050
Cr	360	350	323	582	597	443	1221
Cu	2131	3411	1771	602	683	581	1131
Fe	18,930	20,123	12,980	22,562	22,350	20,890	26,265
K	52,045	46,290	60,030	61,974	71,182	70,050	41,475
Mg	2529	3024	901	20,685	20,218	20,390	11,075
Mn	820	811	876	4274	5327	4296	4856
Na	75,190	76,720	91,410	6905	7590	7940	8485
Ni	94	92	74	95	91	96	76
P	4774	4531	4485	9383	8730	9107	3798
Pb	8143	8688	8204	7876	7590	5152	21,015
S	80,762	70,840	72,500	25,845	25,042	29,250	65,215
Sb	3150	3533	2988	<3	<3	<3	22
Si	101,232	107,883	86,750	144,334	148,950	126,300	129,000
Ti	11,712	11,472	8606	n.a.	n.a.	n.a.	16,535
Zn	44,607	39,810	39,570	12,569	13,047	13,330	21,550
TOC	5190	5750	6010	10,150	17,043	12,030	74,400

Table 3. Mineralogical composition of the analyzed MSWIFA, WWFA40 and WWFA100, determined by XRD.

			MSWIFA			**WWFA40**		**WWFA100**
			wt %			**wt %**		**wt %**
Phases	**Formula**	**MSWIFA_1**	**MSWIFA_2**	**MSWIFA_3**	**WWFA40_1**	**WWFA40_2**	**WWFA40_3**	**WWFA100**
Chlorides								
Halite	NaCl	9	-	14	<1	<1	1	1
Sylvite	KCl	3	3	5	4	4	5	-
K_2ZnCl_4	K_2ZnCl_4	4	3	3	-	-	-	-
Sulfates								
Anhydrite	$CaSO_4$	10	10	11	-	-	-	8
Silicates								
Quartz	SiO_2	3	2	2	10	10	7	5
Gehlenite	$Ca_2Al(AlSi)O_7$	7	5	3	4	2	4	9
Alpha belite	Ca_2SiO_4	4	3	-	5	5	3	3
Albite	$NaAlSi_3O_8$	4	3	3	5	3	5	2
Sanidine	$KAlSi_3O_8$	-	-	-	-	-	-	5
Microcline	$KAlSi_3O_8$	3	4	2	-	-	-	-
Carbonates								
Calcite	$CaCO_3$	5	6	6	17	28	20	8
Magnesite	$MgCO_3$	<1	2	1	-	-	-	7
Ankerite	$CaFeCO_3$	-	-	-	-	1	-	-
Oxides								
Lime	CaO	-	-	-	2	-	4	-
Hematite	Fe_2O_3	<1	1	-	1	<1	<1	1
Rutile	TiO_2	-	-	-	2	1	3	1
Periclase	MgO	1	-	-	3	4	3	-
Mayenite	$Ca_{12}Al_{14}O_{33}$	2	2	3	-	-	-	-
Perovskite	$CaTiO_3$	2	2	2	-	-	-	-
Phosphates								
Monetite	$CaHPO_4$	5	4	3	5	6	5	2
Amorphous		37	41	43	42	35	39	49

3.3. *Acid-Neutralizing Capacity*

Acid-neutralizing capacity (ANC) is similar for ashes of the same type but shows differences between the ash types (Figure 1). The amount mol H^+ needed to reach an optimal extraction pH of 3 varies within 10% and 5%, respectively, for MSWIFA and WWFA40. On average, MSWIFA consumed 4.7 mol H^+, WWFA100 6.2 mol H^+, and WWFA40 with 8.9 mol, almost double the amount of H^+ to reach a pH of 3. The titration curve of WWFA40 is characterized by a small plateau at pH 12.7 and a big plateau at pH 7. Although WWFA100 shows a similarly high initial pH as WWFA40, the ANC titration curve resembles more that of MSWIFA than that of WWFA40, as the plateau starting at pH 7 is less pronounced. The pH starts dropping rapidly from an initial value of 12.7 to pH 7, where calcite buffering starts. For MSWIFA, the initial pH of the titration curve is lower (pH 11.5) and drops rapidly towards pH 5—where an almost linear decrease in pH initiates.

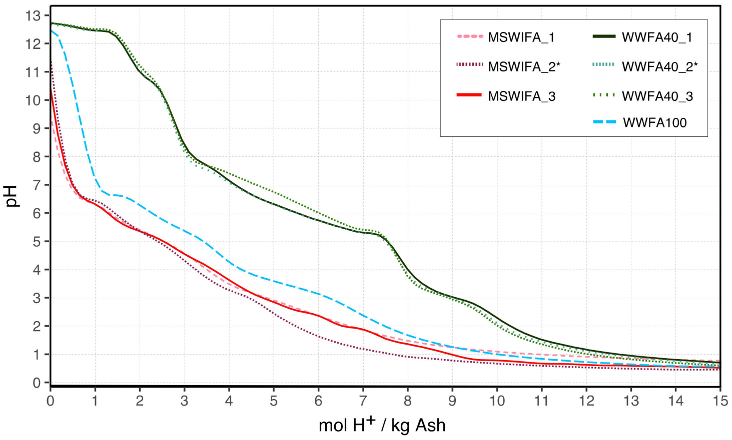


Figure 1. Titration curves of acid-neutralizing capacity (ANC) for MSWIFA, WWFA40 and WWFA100. The samples used for the leaching experiments are indicated with *.

3.4. *Water-Extractable and Total Cr(VI)*

Multiple determination of the water-soluble Cr(VI) concentration of the samples revealed reproducibility within 10%. The Cr(III) spike was fully retained during all eluate tests, which proves that no oxidation of Cr(III) occurred. The Cr(VI) spike was fully retained during the majority of the eluate tests. In the experiments where the Cr(VI) spike was not fully retained, redox transformations leading to the reduction of Cr(VI) occurred (indicated with * in Table 4).

Table 4. Water-extractable Cr(VI) and total Cr(VI) concentrations of WWFA and the filter cakes of WWFA40. Cr(VI) concentrations indicated with * are from extractions with poor Cr(VI) spike recoveries (<2%), implying erroneously low values. Where not indicated, the Cr(VI) spike was fully retained.

	WWFA40						**WWFA100**
	mg/kg						**mg/kg**
	WWFA40_1	**WWFA40_2**	**WWFA40_3**	**WWFA40_4**	**WWFA40_5**	**WWFA40_6**	**WWFA100**
Water-extractable Cr(VI)	58	117	95	83	96	110	1 *
Water-extractable Cr(VI) of filter cake	-	<0.05	-	<0.05	<0.05	0.22	-
Total Cr(VI)	-	1 *	-	-	-	-	87

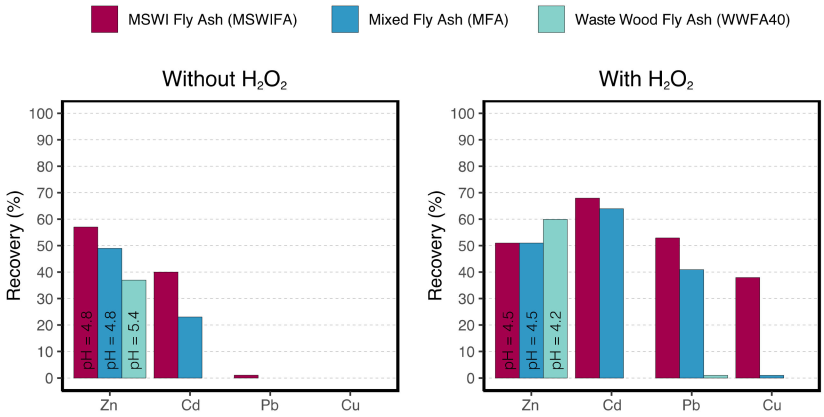
All eluates of the 6 analyzed WWFA40 samples showed water-extractable Cr(VI) concentrations that exceed the threshold limit for landfilling (0.5 mg/kg) by more than two orders of magnitude. The water-extractable Cr(VI) content made up for 10–20%

of the Cr concentration in WWFA40. For WWFA100, the determined water-extractable Cr(VI) concentration was as low as 1 mg/kg. Since the Cr(VI) spike recovery was only 2% for WWFA100, this implies that a major part of the sample's native Cr(VI) also has been reduced. All six analyzed filter cakes from WWFA40, including all filter cakes from the experiments performed in this study, showed Cr(VI) concentrations below the given threshold for landfilling, independent of the applied scale (laboratory or industrial) and the redox conditions.

For the hot alkaline extraction of sample WWFA40_2, none of the Cr(VI) spike was recovered, in neither of the duplicates. The total Cr(VI) concentration was expected to be similar or higher to the measured water-extractable Cr(VI) concentration. Instead, a concentration of 1 mg/kg was measured. For WWFA100, Cr(VI) spike recovery was 80% in the hot alkaline extraction and the measured total Cr(VI) concentration 87 mg/kg. The results of the double determination agreed within 3%. It is assumed that matrix interferences occurred during the hot alkaline extraction of the sample WWFA40_2 (and to a minor extent in sample WWFA100), leading to a strong diminution in Cr(VI) concentration. This might have been favored by the strongly reducing conditions during the hot alkaline extraction with WWFA40_2.

3.5. Laboratory-Scale Leaching Experiments

The heavy metal recovery achieved for the two different experimental setups is shown in Figure 2. The reproducibility of the experiments performed in duplicates was very good (within 5–10%). Only for Cu, the reproducibility was within 20% since the solubility of Cu is strongly pH-dependent, and a small increase in the filtrate pH value can enhance precipitation of Cu hydroxides [21]. Given the attributed uncertainty of 10%, Zn recovery can be considered equal for MSWIFA and MFA, whereas it was lower by 30% for WWFA40. This lower yield is associated with a high leachate pH of 5.4, which assumedly led to Zn precipitation. For Cd, recovery is 40% lower for MFA compared to MSWIFA, whereas no Cd was recovered from WWFA40. No Pb and Cu were mobilized for any of the ash types without the use of H_2O_2.



(**a**) (**b**)

Figure 2. Heavy metal recovery in % for the target heavy metals Zn, Cd, Pb, Cu for the 3 different ash types in laboratory experiments. The pH of the leachate is indicated in the bar for Zn recovery. (**a**) recovery without the use of H_2O_2 (**b**) recovery for experiments with 40 L/t H_2O_2.

When a quantity of 40 L/t H_2O_2 was used, Zn recovery did not change. The recovery for Cd could almost be doubled from MSWIFA, and it was achieved to recover Pb (53%) and Cu (38%). This significantly higher recovery for Pb and Cu (and to a minor extent Cd) when using H_2O_2 was observed in previous studies [14]. The recovery for MFA is equal (within the uncertainty) to that of MSWIFA for Zn and Cd. For Pb, recovery is lower by 25%, and almost no Cu was mobilized during the experiment. For WWFA40, the same recovery for Zn was achieved as for the other ash types, but any of the other heavy metals could be recovered. In the experiment with H_2O_2, the amount of HCl 32% needed to keep extraction pH at a level of 2.5 was twice as high for MFA compared to the experiments with MSWIFA (17 vs. 9 mL, respectively), and the amount needed for WWFA40 was 33 mL.

The ashes showed a strong redox buffer, visible by the subsequent drop in redox potential after each H_2O_2 dosage (Figure 3). For MSWIFA, the redox potential dropped to strongly negative values shortly after the H_2O_2 dosage, whereas for WWFA40, Eh was still positive before the next H_2O_2 dosage. Thus, H_2O_2 consumption seemed to be slower. However, the amount of H_2O_2 added was not enough to maintain oxidative conditions over the entire extraction time for MFA and WWFA40. Only for MSWIFA, it was possible to maintain a stable positive redox potential over the entire experiment with 40 L/t H_2O_2.

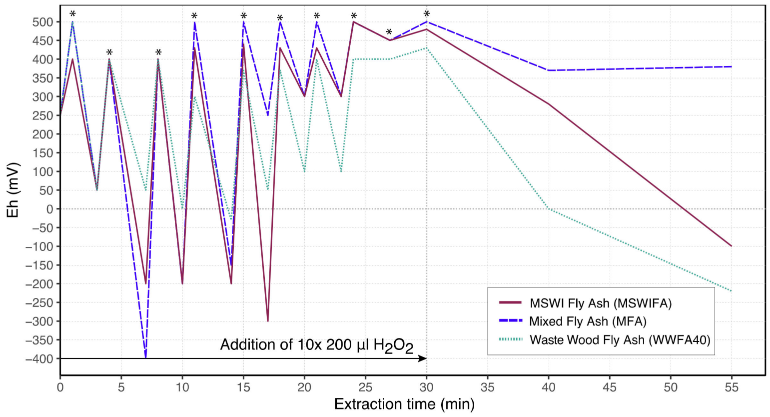
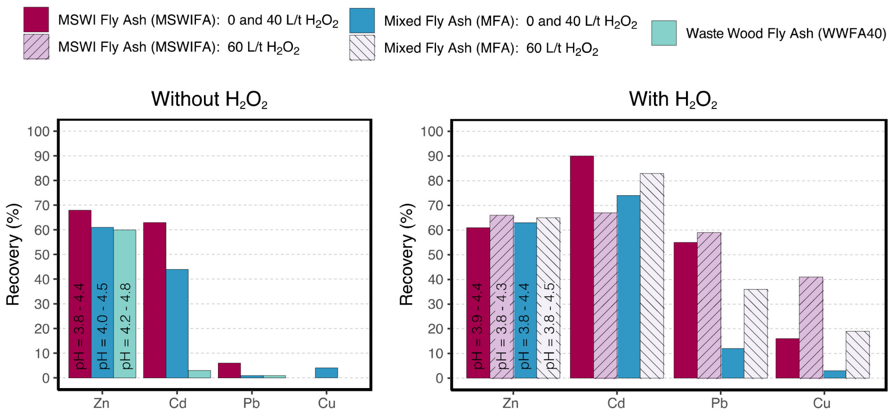


Figure 3. Evolution of redox potential (Eh) during laboratory experiment with H_2O_2. **Left**: Eh before and after each dose of H_2O_2 (indicated with *). **Right**: evolution of Eh after the last H_2O_2 dosage.

3.6. Industrial-Scale Leaching Experiments

Taking into account the attributed uncertainty of 10%, the recovery for Zn was the same for the three ash types independent of the amount of H_2O_2 added. The recovery for Cd reflected the trends observed from the laboratory experiments: a lower Cd recovery by one-third for MFA and a negligible Cd recovery for WWFA40. As already observed in the laboratory experiments, the recovery for Pb and Cu was negligible without H_2O_2 (Figure 4a). With 40 L/t H_2O_2, 55% of Pb and 16% of Cu could be mobilized from MSWIFA, but only 12% Pb and 3% Cu from MFA (Figure 4b). The recovery of both Pb and Cu was thus significantly lower for MFA compared to MSWIFA.



(**a**) (**b**)

Figure 4. Recovery for the industrial-scale experiments (**a**) without and (**b**) with H_2O_2 (40 and 60 L/t H_2O_2). The pH of the leachate is indicated in the bar for Zn recovery. The industrial-scale experiments with H_2O_2 were not performed for WWFA40.

With the higher dosage of 60 L/t H_2O_2, a higher Cd fluctuation in recovery could be observed, but considering the attributed uncertainty of 10%, the recoveries were comparable for the two ash types. For Pb recovery, a strong increase by a factor of three could be observed for MFA, whereas Pb recovery did not increase with the higher dosage for MSWIFA. A clear increase in Cu mobilization could be observed for both ash types, which resulted in recoveries 2.5 and 6 times higher than with 40 L, respectively. Table 5 lists the heavy metal concentrations of the ashes investigated in the industrial-scale leaching experiments. Considerable differences in heavy metal concentrations could be observed, which must be taken into account when comparing the recoveries.

Table 5. Heavy metal concentrations of the different ashes investigated in industrial-scale leaching experiments. The concentrations for the experiments with 40 and 60 L/t H_2O_2 are indicated with * and **, respectively.

	Experiment without H_2O_2				**Experiments with H_2O_2**				
	mg/kg				**mg/kg**				
	Zn	**Cd**	**Pb**	**Cu**	**Zn**	**Cd**	**Pb**	**Cu**	
MSWIFA	44,710	220	6070	1360	43,700	260	10,700	2500	*
					57,350	320	12,910	3090	**
MFA	31,950	170	6760	2010	31,330	190	6460	1970	*
					31,830	160	5710	1770	**
WWFA40	13,890	30	5520	630	-	-	-	-	

4. Discussion

4.1. Chemical and Mineralogical Differences and its Effects on Acid-Neutralizing Capacity

The chemical and mineralogical characterization showed considerable differences between the ash types. As the difference in matrix elements, WWFA showed significantly higher Ca and Si contents and significantly lower concentrations in Cl than MSWIFA. Within WWFA, chemical differences were also observed, depending on the waste wood content. The S content, for example, was as high as in MSWIFA for WWFA100, but less than half the concentration in WWFA40. The fluctuations in the elemental composition of MSWIFA are attributed to the compositional differences in waste input. Remarkable is the constant chemical and mineralogical composition between the different WWFA40 samples, as waste wood is also a very heterogeneous feedstock [22]. This could be an effect of the low waste wood content in WWFA40. The significantly higher Cl concentration in MSWIFA is associated with the combustion of plastics (PVC). It is known that elevated Cl concentrations in the flue gas favor the evaporation and transport of heavy metals (e.g., Cd, Cu, Pb, Zn, Sb [23–25]), and elevated heavy metal concentrations in MSWIFA have been observed by many authors (e.g., [15,26]). The high concentrations of these hazardous metals in MSWIFA are associated with the combustion of, e.g., batteries, paints, alloys, plastics [27]. The high Sb concentrations in MSWIFA are problematic due to their high toxicity (especially of the trivalent species [28]). Antimony is not soluble at the low pH conditions prevailing in the FLUWA process and accumulates in the filter cake. To fully assess the hazard potential of Sb and to evaluate Sb mobilization during the FLUWA process, additional studies are in progress. The high Pb and Cr(VI) concentrations in WWFA are problematic and justify the need for treatment prior to deposition. WWFA100, the WWFA with higher waste wood content, showed significantly higher heavy metal concentrations, which reflects findings made in previous studies on WWFA (e.g., [22]). The elevated Pb and Zn concentration in WWFA is probably due to pigments (e.g., $PbCO_3$, ZnO) from paints and coatings, whereas the high Cu content in WWFA could arise from the combustion of pickled wood products [29].

During combustion, alkali- and alkaline earth metals in the wood transform to oxides and are subject to successive hydrogenation and carbonation during cooling [30], which could explain the high calcite content in WWFA40. The high Si content stands in relation to the usage of quartz sand as bed material during fluidized bed combustion [10]. In the presence of SO_2 and O_2, CaO often forms sulfate compounds (e.g., anhydrite) [31], as present in WWFA100. WWFA100 further showed higher TOC content (associated with incomplete combustion [32]) and different matrix composition (e.g., less calcite, more sulfates) than WWFA40, the latter affecting ANC. The high ANC of WWFA40 can be explained by the very high calcite content and dissolution of Ca-silicates (e.g., gehlenite, belite). The high initial pH of all the three ash types suggests the presence of non- or microcrystalline CaO or $Ca(OH)_2$ since no CaO or lime was identified in all ashes. WWFA100 and MSWIFA both showed poorly acid buffering sulfates and chlorides as main constituents, which explains the lower amount of H^+ needed to reach the acid conditions required for the FLUWA process.

Thus, although WWFA showed different chemical and mineralogical characteristics than MSWIFA, there are also different geochemical properties within WWFA, depending on their waste wood content and certainly also depending on differences in the waste wood composition.

4.2. Water-Extractable and Total Cr(VI) in WWFA and Filter Cakes

The measured average water-extractable Cr(VI) concentration of 93 mg/kg in WWFA40 justifies the strong need for Cr(VI) reduction prior to landfilling. The treatment of WWFA40 with the FLUWA process successfully reduced water-soluble Cr(VI). All analyzed filter cakes showed Cr(VI) concentrations below the threshold limit for landfilling, even when the experiments were performed under oxidizing conditions with H_2O_2. It was shown that acidic conditions are sufficient to dominate the reduction of water-extractable Cr(VI), as also observed in other studies [33]. It was also reported that H_2O_2 could act as a reductant in acidic solutions [34]. It is assumed that the water-soluble Cr(VI) is being reduced to Cr(III) during the FLUWA process, followed by precipitation as Cr(III) phase, probably as hydroxide. This is supported by the absence of dissolved Cr in the filtrate. Unfortunately, no Cr phases could be identified with XRD as the concentrations are very low and the precipitated phases possibly amorphous. It was further shown that the high Cr(VI) concentrations in the eluates were not caused by the oxidation of Cr(III) during the eluate test. However, Cr(VI) reduction occurred during the eluate test for WWFA100 due to its highly reductive character—leading to erroneously low water-extractable Cr(VI) concentrations. Similar matrix interferences occurred during the hot alkaline extraction for WWFA40. These observations show that spiking during Cr(VI) extraction tests with reactive material such as WWFA is indispensable. Poor Cr(VI) spike recovery is not indicative of method failure, but rather an indication for the potential of the sample to reduce the spiked Cr(VI) and not sustain its native Cr(VI) [35]. They further report that the presence of high TOC contents, as well as considerable S^{2-} or Fe^{2+} concentrations in the sample, are most likely the reason for low Cr(VI) spike recovery or reduction of native Cr(VI). Although oxidative conditions prevail during combustion, it cannot be excluded that locally reducing conditions occur, where Fe^{2+} and S^{2-} persist. While no mineral phases containing Fe^{2+} and S^{2-} were observed, their presence in minor concentrations cannot be excluded. For further interpretation, a more detailed investigation on possible reductants other than C_{org} in WWFA must be performed, with special focus on the content of Fe^{2+} and S^{2-}.

4.3. Leaching Experiments: Heavy Metal Recovery and Consumption of Neutralizing Chemicals

The laboratory-scale experiments were able to predict well the recovery trends of the industrial-scale. Differences in the recoveries between laboratory- and industrial-scale are primarily attributed to differences in pH and to element contents of the ash, as well as to a larger L/S in the industrial scale, which will increase the recovery. For WWFA40, a higher H_2O_2 dosage was needed to achieve oxidizing conditions during extraction. This could be caused due to the high content in organic matter or the presence of metals in their metallic form—leading to rapid consumption or even catalytic destruction of the added

H_2O_2. The high ANC of WWFA40 led to higher acid consumption in the FLUWA compared to MSWIFA (3× higher). Thus, WWFA40 can represent a heavy metal-rich replacement for the often-used pH neutralizing agent lime milk. The high acid consumption is even more pronounced when H_2O_2 is used, since the oxidation of, e.g., metallic compounds consumes H^+.

For the element Zn, recovery was equally high for the different ash types independent of the H_2O_2 dosage, as Zn mobility is independent of the redox conditions during extraction but controlled by pH and binding form [36]. The achieved Zn recovery was lower by 15% in the laboratory-scale experiments compared to the industrial-scale experiment. It is assumed that this is due to the higher L/S used in the industrial-scale experiment (L/S of 15 compared to L/S of 3). The low Zn recovery of WWFA40 (laboratory-scale) is associated with enhanced precipitation of Zn due to the high leachate pH. Remarkable is the fact that the Zn recovery seems not strongly affected by the Zn concentration in the ash. As observed in other studies [36], the Zn yield stagnates at about 70% (in this study at about 65% in the industrial-scale-experiments). It is assumed that the majority of the Zn in the ashes is readily available for dissolution (e.g., as Cl- or S-salts). The remaining 30–35% of the Zn seems, however, to be present in the insoluble form under these conditions (e.g., as glassy particles, as Ca replacement in gehlenite or associated with iron [36]). The recovery of Cd showed the same trends for laboratory- and industrial-scale, but with lower recoveries by 15–50% in the laboratory-scale. The higher recoveries at the industrial-scale are again attributed to the higher L/S. The lower Cd yields in the laboratory-scale experiment without H_2O_2 are associated with the higher leachate pH. Since Cd concentration is about one order of magnitude lower than the other elements, it is subject to larger fluctuations as inhomogeneities in Cd concentration in the sample are more pronounced. The low Cd recovery from WWFA40 is attributed to the very low Cd concentration in the ash. An increase in Cd recovery can be observed for each ash type when the experiments are performed under oxidizing conditions, as observed in other studies [36]. As WWFA40 showed a higher redox buffer than MSWIFA, it is assumed that the lower Cd recoveries in the experiments without H_2O_2 are a result of reductive precipitation of Cd since Cd recoveries are comparable to those of MSWIFA when using H_2O_2. The mobility of Pb and Cu is highly dependent on the redox conditions, as well as on the pH (especially for Cu). The recoveries for Pb and Cu for 40 L H_2O_2 are higher on the laboratory-scale than on the industrial-scale. Besides differences in elemental concentrations in the ashes, the pH and redox conditions are more easily controllable on the laboratory-scale than on the industrial-scale. Additionally, the industrial-scale experiment runs over longer timespans and is subject to fluctuations of ash input and neutralizing chemicals. The recoveries for Pb and Cu were significantly lower for MFA compared to MSWIFA, which is attributed to the higher redox buffer of WWFA40. However, further data are required for quantifying the negative effects.

The FLUWA process nevertheless represents a valuable option for treating WWFA as the heavy metal concentrations in WWFA are in the same range as for MSWIFA, and WWFA shows comparable heavy metal recoveries for Zn and Cd. The negative effects of the higher consumption of H_2O_2 affecting the Pb and Cu recovery may be diminished by a cotreatment of lower WWFA ratios.

5. Conclusions

Heat and energy production in Switzerland using waste wood incineration is growing, and new treatment pathways must be implemented to recover heavy metals from the ashes and to reduce Cr(VI) content. Acid leaching, already established for MSWIFA, was found to be a valuable option for the treatment of WWFA. Laboratory-scale experiments were found to be suitable when evaluating the co-processing of MSWIFA and WWFA before implementing at the industrial scale.

Comparison of the chemical and mineralogical composition of WWFA with MSWIFA showed that WWFA could contain heavy metals (especially Pb) in elevated concentrations similar to that of MSWIFA. The investigated WWFA samples showed Cr(VI) concentrations more than two orders of magnitude above the threshold value for landfilling. It was found that the concentrations in heavy metals, Cr(VI) and matrix minerals differed within the two WWFA types, depending on waste wood content. The elevated heavy metal and Cr(VI) concentrations in WWFA justify the need for treatment prior to deposition. The treatment with the FLUWA process allowed to successfully reduce the Cr(VI) in the filter cake until below the threshold value for landfilling, even when the process was performed under oxidizing conditions. The co-processing of WWFA required higher acid dosages due to its high ANC, but the Zn and Cd recovery were not negatively affected by the co-processing. Nevertheless, the co-processing of WWFA had a particularly negative effect on the recovery of the redox-sensitive elements Pb and Cu, as WWFA showed a strong redox buffer and thus a higher consumption of the oxidant H_2O_2. Therefore, higher dosages of H_2O_2 are needed to maintain oxidizing conditions during the process required for Pb and Cu mobilization. The use of a stronger oxidizing agent (e.g., permanganate) could be expedient and should be further tested with regard to successful Cr(VI) reduction. Alternatively, smaller percentages of WWFA could be co-processed in existing FLUWA plants in order to diminish the negative effects due to the higher demand for neutralization chemicals.

Within the next years, the implementation of co-processing the two ash types could contribute significantly to the growing demand for treatment capacities in Switzerland.

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