REDUCTION OF HEXAVALENT CHROMIUM IN ASH FROM BIOMASS UPDRAFT GASIFICATION PLANTS

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ABSTRACT: In this study, different agents for the reduction of hexavalent chromium (Cr(VI)) were evaluated, including $FeCl_2$, $FeSO_4 \cdot H_2O$ (ferrous sulphate monohydrate), as well as water only. Cr(VI) reduction in biomass ashes is of relevance as many ashes exceed the limiting value of Cr(VI) (2 mg/kg d.b.) for the utilization of ashes as a fertilizer. Various dosages of the reducing agents were applied to grate ash obtained from a commercial biomass updraft gasification plant. In addition, the influence of the moisture content of the ash (20 and 30 wt%, wet basis) was systematically investigated. All experiments were conducted at pilot scale using a commercial concrete mixer. Cr(VI) concentrations were determined immediately after mixing the ash with the reducing agents at different multiples of the stoichiometric requirement, as well as after storage periods of 5 and 10 weeks. Sampling and analytical procedures were performed in accordance with relevant ISO standards. Cr(VI) was quantified following EN 16318 (Method A). Major elements were analyzed by ICP-OES, while trace elements were determined by ICP-MS.
The addition of water without any reducing agent seems to have no strong influence on the reduction of Cr(VI). The reducing agents iron sulphate and iron chloride immediately reduce the Cr(VI) content significantly. Regarding the water content of the ash, 30% water could help to obtain higher efficiencies of Cr(VI) removal but may cause problems regarding ash agglomeration, therefore, 20 wt% water seems more suitable. In general, iron sulphate works better than iron chloride. Cr(VI) tends to increase again as a function of storage duration. This fact is important because ash usually needs to be stored for a certain time before it can be applied. Therefore, this "time effect" also needs to be considered, it is most likely caused by the generation of OH^- ions due to the basicity of the ash, which shifts the equilibrium over time.
Keywords: ash, biomass, biofertilizers, characterization, toxicity

1 INTRODUCTION AND BACKGROUND

Despite the fact that various options for the utilization of biomass ashes exist, most biomass ashes produced have been landfilled in the past, due to the lack of appropriate legal regulations for the use of biomass ashes as a nutrient or a liming agent [1]. Biomass ashes contain significant amounts of plant nutrients such as K, Mg and P, as well as considerable levels of Ca (relevant for liming). Therefore, the application of biomass ashes on agricultural land could help to close mineral cycles and partially replace chemical fertilizers, contributing to the sustainable use of bioenergy and promoting a circular economy approach.

Reducing the use of chemical fertilizers is essential to lower energy consumption and mitigate the environmental impacts associated with conventional agricultural practices. In this context, the European Fertilizer Regulation (EU 2019/1009) has been revised to allow biomass ash to be used as a raw material in fertilizer production. However, this regulation limits the Cr(VI) content to 2 mg/kg. While compliance with limits for other heavy metals is relatively straightforward when chemically untreated wood is used, typical Cr(VI) concentrations in bottom ash from biomass combustion and updraft gasification plants range from 0.5 to over 40 mg/kg [2]. Studies show that there is no correlation between the total Cr content and the Cr(VI) content in biomass ashes [3,4]. This highlights Cr(VI) as the primary challenge for the use of biomass ash in fertilizers.

Consequently, the development of a reliable and cost-effective method to reduce Cr(VI) concentrations below the regulatory limit would represent a crucial step towards increasing the utilization of biomass ash as fertilizer.

Based on literature, different approaches have been investigated in the past.

The addition of formaldehyde [5] to the wet ash removal process can improve the efficiency of Cr(VI) reduction, but due to the toxicity of formaldehyde (formaldehyde can cause allergies, skin, respiratory or eye irritation if used incorrectly; chronic exposure is carcinogenic and impairs memory, concentration and sleep), this method has not been used in industrial applications yet.

Thermal treatment can reduce the Cr(VI) concentration in biomass ashes, as demonstrated by [6], but as sufficient treatment requires temperatures of about 650°C for 20 min, the additional operating costs for such a treatment are too high. Another study [7] recommends even higher temperatures up to 1000°C. Thus, this treatment method has also not been used in industrial applications yet.

The admixing to compost can efficiently reduce Cr(VI) contents in wood ashes [2], but this treatment does not allow for a further use of the ash as a raw material for fertilizer production, since the ash remains dispersed in the compost and requires further investigation.

Investigations on fixation of Cr(VI) in the ash or its extraction showed a slight reduction of the Cr(VI) content but no reliable reduction of the Cr(VI) content in the ash could be achieved [3].

In contrast to the methods discussed, the reduction of Cr(IV) with Fe(II)-salts is a proven process that has been used in the cement industry for many years and several trials with wood ash confirmed its suitability [2,3]. Commonly used Fe(II) salts are Fe(II) sulphates and Fe(II) chlorides. A stoichiometric dosage is generally not sufficient; instead, the optimum dosing rate of the reducing agent should be determined in each individual case by means of laboratory tests. From R&D projects already performed with biomass ashes an overdosage of 20 to 30 times the stoichiometric amount seems to be

reasonable. The water content of the mixture shall be in the range of 20 to 30 wt% [2].

The general main reactions are:

$FeSO_4$ (aq) → $Fe^{2+} + SO_4^{2-}$; $Fe^{2+} + 2\ OH^-$ → $Fe(OH)_2$

$FeCl_2$ (aq) → $Fe^{2+} + 2\ Cl^-$; $Fe^{2+} + 2\ OH^-$ → $Fe(OH)_2$

$CrO_4^{2-} + 3\ Fe(OH)_2 + 4\ H_2O$ → $Cr(OH)_3 + 3\ Fe(OH)_3 + 2\ OH^-$

For an effective Cr(VI) reduction in the ash, a thorough mixing of all components is essential, as the elution of Cr(VI) is significantly slower than the competing reaction of Fe(II) by dissolved atmospheric oxygen. Without the intense contact between ash, reducing agent and water, the oxidation of Fe(II) by atmospheric oxygen will be favored over the oxidation of Fe(II) by Cr(VI) [8].

Due to the high pH level of the ashes, successfully reduced Cr may undergo a reverse reaction in high humidity and the abundance of atmospheric oxygen, but a thorough mixing of the ash with the reducing agent and water should keep this to a minimum [8].

The objective of this study is to reduce hexavalent chromium in ash from biomass updraft gasification plants to levels below the limit established by European Union regulations, enabling its use as a fertilizer.

2 MATERIALS AND METHODS

2.1 Ash and ash sampling

A bulk ash sample (1000 kg) was collected from a commercial biomass updraft gasification plant coupled with a gas burner located in Austria, and transported to CEDER-CIEMAT for hexavalent chromium reduction experiments.

Upon arrival of the ash, it was blended by creating a longitudinal pile as shown in Figure 1. The pile was divided into 20 fractions. 10 fractions were used for the 10 reducing tests according to the experimental design (see next section 2.2). A representative sample was taken for analysis (see section 2.4) to calculate the dosage of reducing agents (ferrous sulfate monohydrate and ferrous chloride).



Figure 1: Longitudinal pile of ash

2.2 Experimental design for Cr(VI) reduction.

Based on the considerations outlined in the introduction, ferrous sulphate monohydrate and ferrous chloride were selected as reducing agents and evaluated at two dosage levels: 20 and 30 times the stoichiometric requirement against variants with water addition only (see Figure 2). For each dosage level, two moisture contents (20% and 30%, wet basis) were tested, summing up to a total of 10 subtests.

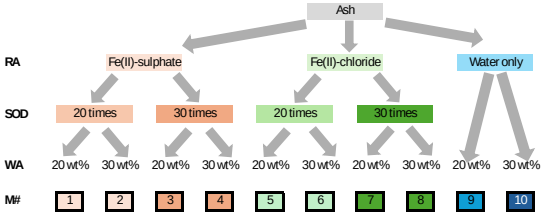


Figure 2: Experimental design to reduce Cr(VI) in the ash

Explanations: RA … reducing agent; SOD … stochiometric overdose; WA … water addition based on wet basis; M# … mixture number.

2.3 Ash blending and storage procedures

Each ash fraction (approx. 50 kg) was processed in a concrete mixer (Figure 3). The reducing agent was first dissolved in water and subsequently added to the ash. The addition of water, reducing agent and ash was completed within 5–7 minutes, followed by continuous mixing for 10 minutes at 30 rpm.



Figure 3: Concrete mixer and prepared ash

Following, the wet mixture was poured onto the clean, dry ground and divided into 9 fractions (Figure 4) for initial analysis and ash storage for 5 and 10 weeks (3 replicates for the initial sample and each storage period).

For storage, the prepared ash was placed in polypropylene tubes with a height of 1.6 m and an internal diameter of 7.5 cm (Figure 5), to simulate the conditions in an ash container, where only the surface of the ash has direct access to air.



Figure 4: Division of the prepared ash



Figure 5: Storage of prepared ash in the pipes

2.4. Analytical procedures

The physical and chemical characterization of the ash was carried out at the Biomass Characterization Laboratory of CEDER-CIEMAT. The analytical methods applied are summarized in Table I.

Table I: Analytical methods applied for physical and chemical characterization of the ashes

Property	**Analytical method (equipment)**
Moisture	Drying at 105 ºC
Unburnt material	Ashing at 550 ºC
C, H, N	Elemental analysis (Leco, TruSpec)
TOC/TIC	Carbon analysis (Elementar, SoliTOCcube)
Cl	Leaching with ultrapure water and ion chromatography (Methrom)
Major elements in ash	Microwave digestion followed by ICP-AES (Thermo Fisher Scientific, Jarrell Ash Iris/AP)
Minor elements (As, Cd, Cr, Cu, Ni, Pb and Zn)	Microwave digestion followed by ICP-MS (Thermo Fisher Scientific, iCAP Q)
Mercury	Gold amalgamation followed by AAS (Milestone, DMA-80)
Cr(VI)	Photometer Hach (DR 3900)
Inorganic phases	XRD (PANalytical, X'Pert-PRO)

Cr(VI) concentrations in ash were determined according to Method A of EN 16318:2016, which is specifically developed for fertilizers and liming materials. In brief, the method involves extraction (elution) with deionized water for 15 minutes at room temperature, followed by photometric determination using diphenylcarbazide as an indicator. The method is applicable for Cr(VI) concentrations above 0.1 mg/kg in solid samples.

3 RESULTS AND DISCUSSION

The physical and chemical characterization of the ash from the updraft gasification plant is presented in Table II. The carbon content is predominantly inorganic, with a TIC of 1.5% d.b., very similar to the total carbon content (1.8% d.b.), while only 0.1% d.b. of organic carbon was determined. The major elements in the ash are SiO_2 and CaO, with 30% d.b. and 28% d.b., respectively (expressed as oxides), followed at a distance by K_2O with 11% d.b. According to the results of semi-quantified crystalline phases by X-ray diffraction, calcium is mainly present as calcite, followed by lime, although it is also combined with SiO_2 in the form of akermanite. K2O is found combined with SiO_2 in the form of kalsilite.

The amount of trace elements in the ash seems typical for ash from biomass combustion using chemically untreated biomass fuels. Cr(VI) has a content of 7.9 ppm d.b. This is well within the range documented in literature [2].

Table II: Analysis results of the ash used in the tests
Explanations: units in dry basis, except for moisture in wet basis; ND: not detected.

Sample Averaged	**Moisture** (%)	**C** (%)	**H** (%)	**N** (%)	**TOC** (%)	**TIC** (%)	**Cl** (%)
Ash	0.3	1.8	<0.5	<0.10	0.1	1.5	0.02

Sample Averaged	**Al_2O_3** (%)	**CaO** (%)	**Fe_2O_3** (%)	**K_2O** (%)	**MgO** (%)	**Mn_2O_3** (%)	**Na_2O** (%)	**P_2O_5** (%)	**SO_3** (%)	**SiO_2** (%)	**TiO_2** (%)	**Sum**
Ash	5.5	28	2.4	11	4.5	0.83	1.0	2.6	1.4	30	0.34	87.8

Sample Averaged	**As** (mg/kg)	**Cd** (mg/kg)	**Cr** (mg/kg)	**Cr VI** (mg/kg)	**Cu** (mg/kg)	**Hg** (mg/kg)	**Ni** (mg/kg)	**Pb** (mg/kg)	**Zn** (mg/kg)
Ash	6.1	0.23	51	7.9	70	0.004	54	1.1	44

Sample Averaged	Silica SiO_2 (%)	Sylvine KCl (%)	Calcite $CaCO_3$ (%)	Lime CaO (%)	Kalsilite $KAlSiO_4$ (%)	Akermanite $Ca_2MgSi_2O_7$ (%)
Ash	10	ND	37	5	39	9

According to the experimental design (see Section 2.2), the Cr(VI) removal results for each subtest are presented in Figure 6. As observed, the addition of water alone does not achieve the same level of Cr(VI) reduction as treatments with ferrous sulfate or ferrous chloride.

Ferrous chloride appears to be less effective than ferrous sulphate in reducing Cr(VI). The reason for this cannot be explained as both $FeCl_2$ (available in liquid form) and $FeSO_4$ (available in solid form but first mixed with water and solved in water before mixed with the ash) are applied in liquid form. Further evaluation in additional tests is therefore needed.

Figure 6 also illustrates the effect of ash storage over 5 and 10 weeks, as described in Section 2.3. An increase in Cr(VI) concentrations with storage time is observed. This behaviour can be explained by the following redox equilibrium:

$$CrO_4^{2-} + 3\ Fe(OH)_2 + 4\ H_2O \rightleftharpoons Cr(OH)_3 + 3\ Fe(OH)_3 + 2\ OH^-$$

The generation of OH^- ions shifts the equilibrium to the left, favouring the formation of Cr(VI) (CrO_4^{2-}) from Cr(III) ($Cr(OH)_3$). This is consistent with the alkaline nature of the ash, which promotes OH^- formation, particularly in the presence of added moisture. Additionally, oxygen diffusion during storage may contribute to the re-oxidation of Cr(III) to Cr(VI), as suggested in previous studies [9]. This effect is likely enhanced by the open-top design of the storage pipes, which facilitates oxygen ingress.

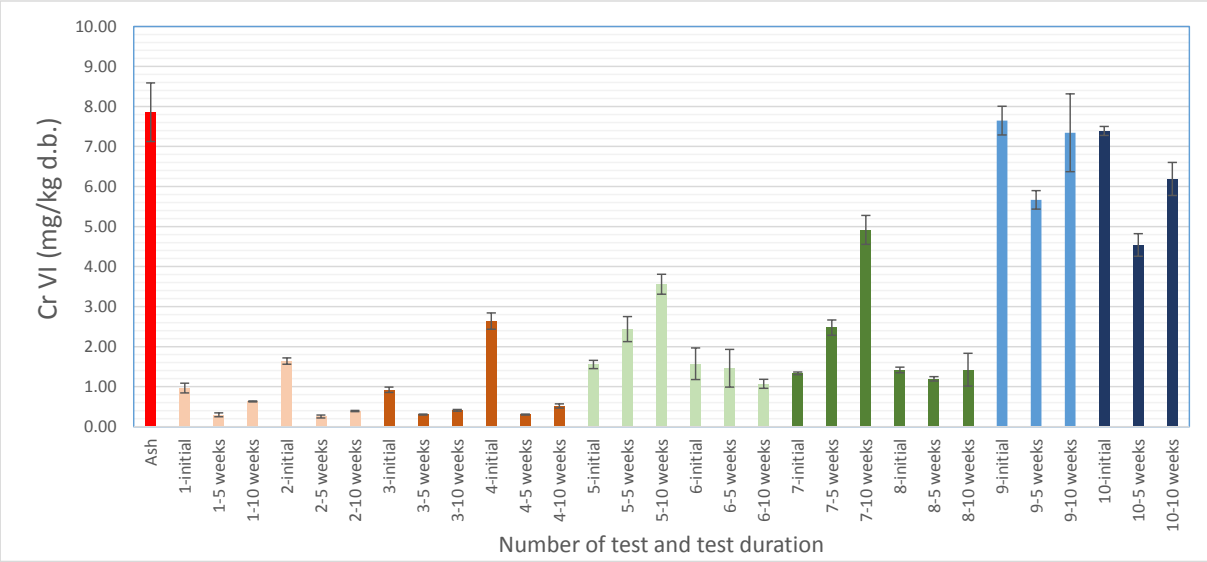


Figure 6: Results of the storage tests with different reducing agents + water and water only Explanations: #-x-weeks … # number of mixture, analysis x weeks after mixture; see also Fig. 2 for explanation of the individual mixtures.

Increasing the dosage of reducing agents from 20 to 30 times the stoichiometric requirement does not appear to significantly improve Cr(VI) reduction.

Furthermore, tests conducted at 30% moisture content led to the formation of larger agglomerates after 5 and 10 weeks of storage. This significantly complicated sample handling and required additional grinding prior to analysis, thereby increasing operational complexity and cost. However, further tests are needed to confirm these results.

Some results shown in Figure 6 are less straightforward to interpret. For example, the relatively high Cr(VI) concentration observed in test 4 which could be attributed to localized oxidation effects within that specific ash fraction. This could occur despite thorough homogenization, subdivision into 20 fractions, and careful sampling performed with the prepared ash from the concrete mixer.

Another unexpected result is the lower Cr(VI) concentration at week 5 compared to the initial value in tests 9 and 10 (water-only treatments). One possible explanation could be the presence of partially oxidized metals in the ash, which may exert a reducing effect similar to that of $FeCl_2$ or $FeSO_4$.

4 CONCLUSIONS AND OUTLOOK

The following conclusions can be taken from the results of the tests described above:

- The addition of water alone does not seem to have a strong influence on the reduction of Cr(VI).
- The addition of 30% water in combination with a reducing agent could help to obtain higher efficiencies of Cr(VI) removal compared to 20% but may cause problems regarding ash agglomeration. Further evaluation regarding the optimum water addition rate is recommended.
- Ferrous sulfate seems to be more effective than ferrous chloride for Cr(VI) reduction in ash from biomass updraft gasification. All four different mixtures with $FeSO_4$ showed a reduction of the Cr(VI) content below the limiting value of 2 mg/kg. Mixtures with $FeCl_2$ only showed a reduction below the limiting value in combination with 30% water and the Cr(VI) concentrations achieved are on a higher level than for $FeSO_4$.
- Cr(VI) tends to increase again as a function of the storage duration. This is important because ash is usually stored for a certain time before it can be applied. Therefore this "time effect" also needs to be considered, it is most likely caused by the generation of OH^- ions due to the basicity of the ash, which shifts the equilibrium over time. Following, further evaluations are needed regarding this subject.

Outlook: further tests are planned with ashes with different Cr(VI) contents to develop an appropriate treatment strategy (dosage rate + water addition).

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7 LOGO SPACE