

1 **WATER LEACHING OF HERBACEOUS BIOMASS BALES TO REDUCE**
2 **SINTERING AND CORROSION**

3 Miguel J. Fernández ^{a,*}, Veronika Chaloupková ^b, Ruth Barro ^a

4
5 ^a Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT)

6 CEDER-CIEMAT (Energy Department), Autovía A-15, sal. 56 - 42290 Lubia, Soria (Spain)

7 ^b Czech University of Life Sciences Prague, Faculty of Tropical AgriSciences, Kamýcká 129,
8 Prague 6, 165 21 (Czech Republic)

9
10 *Corresponding author, Tel: +34 975 281013, Fax: +34 975 281056, Email:

11 miguel.fernandez@ciemat.es

12
13
14 **ABSTRACT:**

15 Two different leaching treatments (immersion and irrigation) were applied to the biomass bales
16 of two different herbaceous solid biofuels (barley straw and tall wheatgrass) in order to improve
17 their sintering and corrosion behaviour during combustion. Six immersion treatments (1 h with
18 and without stirring, and 5 h, 1 day and 2 days without stirring) and two irrigation treatments
19 with tap water (900 L and 1800 L) were tested. The bales made of barley straw were of high-
20 density 140 kg/m³) whereas the density of tall wheatgrass bales was lower (80 kg/m³). After
21 the leaching treatment, bales were dried naturally indoors. Sintering and corrosion tests along
22 with chemical elemental analyses, X-ray diffraction and SEM analyses were performed on the
23 lixiviated biomass.

24 An immersion treatment of 5 h reduced the sintering and corrosion potential of both types of
25 bales to an acceptable level. In high-density bales, the irrigation treatment (1800 L) provided

1 similar sintering and corrosion reductions than those obtained when the 5 h immersion
2 treatment was applied. However, in low-density bales, the immersion treatments provided much
3 better results than irrigation leaching systems, probably in connection with their different
4 degrees of compaction. The naturally drying process of the lixiviated bales can be considerably
5 long, particularly after immersing high-density bales. The drying period to reach a moisture
6 level of 20% w.b, was longer than 100 days for high-density bales and shorter than 20 days for
7 low-density bales.

8
9 **Keywords:** biomass, leaching, corrosion, sintering, drying, chemical composition.

10 11 12 13 14 **1 INTRODUCTION**

15
16 Biomass is postulated as the main source of renewable energy to produce heat and electricity
17 where a deficit of wind or sun energies exists. However, good quality biomass, mainly of woody
18 origin, tends to increase the energy price [1] and thus other sources of biomass should also be
19 considered. According to their origin and physical and chemical properties, biomass derived
20 sources can be divided into: woody, herbaceous, agro-industrial, animal, human, and aquatic
21 biomass, as well as the organic fraction of urban or industrial wastes. Among all these origins
22 and sources, the herbaceous biomass might be the best solution due to its abundance and
23 relatively good properties such as their moisture content and calorific value.

24
25 Nevertheless, the herbaceous biomass might generate environmental problems derived from the

1 emission of particles, sulphur oxides and nitrogen oxides, as a consequence of its significant
2 levels of ash, S and N, respectively. In general, herbaceous biomass is rich in alkaline
3 compounds and is prone to cause technical problems in power plants such as fouling, slagging
4 and corrosion when compared with the biomass of woody origin.

5

6 Several solutions have been proposed to reduce corrosion and sinter formation in the thermo-
7 chemical processes of herbaceous biomass, including biomass leaching [2-5], the use of mineral
8 additives, co-combustion with other fuels [5-9], decreasing the combustion temperature [5],
9 or even a combination of processes such as pyrolysis followed by combustion [10]. The
10 selection among all the available options will depend not only on the cost of the process but
11 also on the efficiency of the occurring chemical reactions.

12

13 Laboratory tests on biomass leaching are very promising since they are highly effective in
14 modifying the composition of the fuel by removing water soluble compounds. It is due to the
15 intimate contact that is reached between water and biomass, which can even be enhanced by
16 prolonging extraction times, applying agitation or reducing the particle size of the fuel.
17 However, with the exception of field leaching [2-3,9,11], most of these methods have been
18 barely studied, particularly when it comes to real field applications in pilot plants or on an
19 industrial scale. To the best of the authors' knowledge, industrial plants based on biomass water
20 leaching do not exist.

21

22 One of the main problems of straw field leaching is the lack of rainwater needed to lixiviate
23 alkaline elements, which might be a particularly severe issue in certain environments such as
24 marginal lands suffering from water scarcity. Additional problems have been reported in the
25 literature when using this field leaching treatment, such as sand contamination from soil, straw

1 losses derived from strong winds, or the loss of organic material as a result from biomass
2 decomposition [11]. Moreover, biomass field drying could take long time and can be further
3 extended when it rains. On the other hand, field leaching avoids the equipment costs needed
4 when subjecting the fuel to a wetting treatment at a facility site [11] and might reduce the
5 fertilisation inputs, as nutrients from leachates are able to return to soil.

6

7 In this work, different straw leaching treatments are studied in a pilot plant facility in order to
8 reduce sintering and corrosion while avoiding the problems which may arise during field
9 leaching, such as rainwater deficits, material losses or biomass contamination with soil
10 particles. The procedures proposed could be performed in industrial facilities prepared for this
11 purpose, which could be located either in the field or at a power plant. Two different leaching
12 treatments (immersion and irrigation) were studied under different conditions using low and
13 high density straw bales. In addition, the drying process of bales after being leached was
14 monitored indoors under natural ventilation.

15

16

17

18

19

2 MATERIALS AND METHODS

2.1 Biomass and solid biofuels

Two herbaceous biomass feedstocks were used: barley (*Hordeum vulgare*) straw from a traditional crop and tall wheatgrass (*Elytrigia elongata*) from an energy crop. The whole of the plant above ground (without roots,) of tall wheatgrass was used for baling.

Biomass was harvested, pressed and tied into rectangular bales and air dried naturally. Physical characteristics of the bales are shown in Table 1. High-density bales were reached in case of barley straw (137 kg/m³) and low-density bales (80 kg/m³) were produced in the case of tall wheatgrass. The bales were stored indoors under natural ventilation until treatment.

Table 1: Bale characteristics

2.2 Leaching treatments

Two different leaching treatments (immersion and irrigation) were tested using tap water at room temperature (Figure 1).

During the immersion treatment, bales were submerged in a plastic container, which was previously filled with 900 L of tap water. Bales were kept submerged with the help of a weight.

Four different immersion conditions were tested: 1 hour, 1 hour with stirring, 5 hours, 1 day

1 and 2 days. In case of the experiment that involved stirring, water was agitated with a shovel
2 for 1 minute and every 5 minutes.

3
4
5
6 **Figure 1:** Scheme of the two different bale leaching treatments

7
8 During the irrigation treatment, bales were rinsed using 900 or 1800 litres of tap water (Figure
9 1 and Table 2). Bales were placed on a pallet, which was located on the upper part of the
10 container used for water collection. Water was evenly sprayed on the upper surface of the bale
11 with a garden sprayer (head diameter of 5 cm), starting from one edge of the bale and ending at
12 the opposite edge until the surface of the bale was entirely showered. In the case of 900-litre
13 irrigation, every bale was irrigated twice with a total volume of 450 litres per irrigation. This
14 process lasted 90 min per each 450 litres. Consequently, in the case of 1800-litre irrigation,
15 each bale was irrigated four times with a total duration of 6 hours.

16
17 **Table 2:** Leaching treatments

18
19
20
21 Bales were weighed before and after being lixiviated. Water conductivity in the container was
22 monitored in order to control the leaching process. Biomass samples were extracted from bales
23 by using a hook and following the international standard for sampling solid biofuels (ISO
24 18135:2018). Three subsamples were taken from different positions of each bale before being

1 treated and three more subsamples were extracted after lixiviation. Subsamples were mixed to
2 form a combined sample for testing.

6 **2.3 Physical and chemical tests**

8 Biomass and ash analyses were carried out following current ISO standards for solid biofuels.
9 The analytical techniques and standards used are listed in Table 3.

11 Biomass ashes, which were obtained at 550 °C, were acid digested in a microwave furnace
12 using HNO₃, H₂O₂ and HF as a first step and H₃BO₃ as a second step before being further
13 analysed by ICP-OES (Thermo Jarrell Ash) in accordance with ISO 16967:2015.

15 X-ray diffraction analyses were performed using a PANalytical X'pert-PRO diffractometer
16 operating at 45 KV and 45 mA. The mineral phases of the biomass ashes (obtained at 550 °C
17 following ISO 18122:2015) were identified by means of the Inorganic Cristal Structure
18 Database (ICSD, Fiz Karlsruhe, Germany). Semi-quantification was performed using Rietveld
19 analysis and results were normalised.

21 Ash melting behaviour was determined according to ISO 21404:2020 [12] and using an optical
22 heating microscope (Hesse Instruments). The following three characteristic temperatures were
23 reported: deformation temperature (DT), hemisphere temperature (HT) and fluid temperature
24 (FT).

1 **Table 3: Standards and analytical methods**

2
3
4
5 In addition, the earth-alkaline to alkaline oxides ratio (I) was also used to predict ash melting
6 behaviour. This predictive index was previously developed by CIEMAT and tested successfully
7 in different solid biofuels [13]. Index I is calculated as follows:

$$8 \quad I = (\text{CaO} + \text{MgO}) / (\text{K}_2\text{O} + \text{Na}_2\text{O})$$

9 The ash melting behaviour improves as I increases. In general, ashes with I values higher than
10 2 should not present sintering risks at the normal operating temperatures of a biomass
11 combustor.

12 13 14 15 **2.4 Corrosion tests**

16
17 To predict how the lixiviation process could have affected the corrosion behaviour of the
18 biomass, a corrosion test at laboratory scale was performed on the ashes of the leached biomass.
19 Ashes were obtained from the biomass of the lixiviated bales at 550 °C following ISO
20 18122:2015 and placed on rectangular steel bases (20 mm x 10 mm, 2 mm thickness) as it is
21 shown in Figure 2. The selected steel was Fe-2.25Cr-1Mo. The steel coupons were previously
22 polished with sandpaper numbers 220, 500, and 1200, and cleaned with acetone. Ashes (50 mg
23 per sample) and steel coupons were placed on a sample holder which was able to accommodate
24 18 samples, and then introduced in a tubular furnace at 700 °C for 200 h with a continuous air
25 flow at 150 mL/min (Figure 2).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

Figure 2: Schematics of the corrosion test using a tubular furnace.

Before SEM-EDX (Scanning Electron Microscopy - Energy Dispersive X-ray spectroscopy) analysis, the steel coupons were embedded in resin, cut with a precision cut-off machine (Struers Secotom-10) using an Al₂O₃ disc and a mineral oil like refrigerant, polished with sandpaper number 1200 and washed with hexane in an ultrasound bath.

The steel thickness and the elemental composition of the metal/corrosion interface were measured by SEM-EDX using a Zeiss instrument (Evo LS-10).

2.5 Bale drying and meteorological conditions

Wet bales were stored indoors under natural ventilation throughout most of the summer (from May to September). Each bale was placed on a pallet for easy handling and transportation and to speed up the drying process. The moisture content was determined as a difference between final and initial mass using a digital hanging crane scale.

Tests were performed in Soria (central-northern Spain). According to Köppen-Geiger classification, the climate at the experimental site is considered to be temperate with a dry season and mild summer (Cfb). During the bale drying study period (from May to September),

1 a mean temperature of 19 °C and maximum temperatures considerably above 30 °C were
2 registered, with a maximum absolute temperature of 35.3 °C. Mean ambient relative humidity
3 was 63%.

4

5

6

7

8

3 RESULTS AND DISCUSSION

3.1 Physical and chemical composition of the baled biomass

Table 4 shows the calorific values and the proximate and ultimate analysis of the baled biomass, together with the ash fusibility temperatures and their ash chemical composition.

Tall wheatgrass calorific value (mean net calorific value of 17.44 MJ/kg d.b.) is higher than for barley (16.25 MJ/kg, d.b.) due to its higher C and H contents and its lower ash content (4.3% vs. 7.1%).

In spite of the similarity of the chemical composition of both types of ashes, with comparable SiO₂, K₂O and CaO levels, their deformation and fluid characteristic temperatures differed by 100 °C, probably in connection with their different Cl content, which is higher in barley straw (0.62 wt.%) than in tall wheatgrass (0.18 wt.%). Consequently, the proportion of KCl is higher in barley than in tall wheatgrass, as it was demonstrated by XRD analysis (see Section 3.2). In contrast, barley exhibits lower S contents (0.06 %) than tall wheatgrass (0.10 wt.%). It is well known that the melting temperature of KCl (775 °C) is lower than K₂SO₄ (1045 °C). This could be the reason why barley straw sinters and melts at lower temperatures than tall wheatgrass.

Table 4: Characterisation of the barley and tall wheatgrass baled biomass.

d.b.: dry basis; GCV: gross calorific value at constant volume; NCV: net calorific value at constant pressure;

ND: not determined

1

2 **3.2 Effect of leaching on the chemical composition**

3

4 The concentrations of K, Cl and S of the baled biomass were analysed before and after applying
5 the leaching treatments considered, and the results are shown in Figure 3 for tall wheatgrass
6 bales and Figure 4 for barley straw bales.

6 .

7

8

9

10 **Figure 3:** S, Cl, and K concentrations on the baled tall wheatgrass biomass according to the
11 leaching treatment.

12

13

14

15 **Figure 4:** S, Cl, and K concentrations on the baled barley straw biomass according to the
16 leaching treatment.

17

18 K and Cl decreased notably with immersion time. The highest K, Cl, and S leaching efficiencies
19 were noticed when bales were submerged for 1 day. Longer immersion times (2 days) were not
20 able to leach higher amounts of K, Cl, and S from the baled biomass. In addition, the leaching
21 of these elements was also not affected positively by water stirring.

22

23 After being immersed for 1 day, contents of 0.21% of K (74% of K reduction), 0.03% of Cl
24 (83% of Cl reduction), and 0.06% of S (39% of S reduction) were measured for the biomass of
25 tall wheatgrass, whereas the biomass of barley straw showed levels of 0.18% of K (86% of K

1 reduction), 0.06% of Cl (90% of Cl reduction), and 0.03% of S (58% of S reduction).

2
3 Even though the content of S present in the baled biomass was clearly reduced after leaching,
4 these levels decreased to a lower extent than K and Cl, probably in connection with the lower
5 solubility of arcanite (K_2SO_4) when compared to sylvine (KCl). Specifically, the solubility of
6 KCl in cold water at 20 °C is 340 g/L, much higher than that of K_2SO_4 (120 g/L).

7
8 The efficiency of K leaching when tall wheatgrass bales were irrigated was lower than when
9 bales were submerged, showing reductions of 21% vs. 74% for 1-day immersion. Additionally,
10 when applying the irrigation treatment to this type of bale, the conductivity increase of the
11 leached water, when compared to the tap water used for irrigation, was negligible. The lower
12 K reductions observed when this type of bale were irrigated, when compared to being
13 submerged, are probably connected to its low density, which does not foster the contact between
14 the biomass fibres and the irrigation water.

15
16 In contrast, irrigation seems to have affected the K content of barley straw bales to a higher
17 extent than tall wheatgrass bales. K reductions of 49% and 67% were noticed when irrigating
18 barley bales with 900 and 1800 L, respectively. The higher grade of compaction of barley straw
19 bales seemed to favour this interaction by trapping water inside the bale, which could have
20 caused a more intimate contact of the biomass with the water embedded in the bale. In any case,
21 5-hour to 1-day immersions seem to be the most efficient treatment to leach the soluble
22 elements present in this type of biomass and bale.

23
24 Figures 5 and 6 show the mineral compounds of tall wheatgrass and barley straw ashes,
25 respectively, according to the leaching treatment. As can be seen in these figures, the

1 concentration of KCl present in barley ashes was higher than that contained in tall wheatgrass,
2 whereas K₂SO₄ levels were found to be higher in tall wheatgrass ashes, which is also related to
3 the different fusibility behaviour of the two biomasses studied (section 3.1).

4
5 On the other hand, it should be mentioned that calcinite (KHCO₃) was only detected in the ashes
6 of tall wheatgrass bales before leaching. This compound was not detected once these bales were
7 leached, probably as a consequence of the low concentration in the original bale together with
8 its relatively high water solubility (220 g/L).

9
10
11
12 **Figure 5:** Ash inorganic compounds of tall wheatgrass bales according to the leaching
13 treatment (XRD analysis)

14
15
16
17 **Figure 6:** Ash inorganic compounds of barley straw bales according to the leaching treatment
18 (XRD analysis)

19
20 In summary, the extent to which the water soluble compounds are leached will depend not only
21 on the solubility of the inorganic compounds contained in the biomass ash and the type and
22 conditions of the applied leaching treatment, but also on bale density.

3.3 Effect of leaching on ash melting behaviour

The predictive empirical index I (see section 2.3) is shown in Figure 7 as a function of the leaching treatment for the two types of bales studied. Higher indices were obtained for those samples characterised by lower K contents.

As mentioned in section 2.3, it was previously demonstrated that, in general, biomasses with earth-alkaline to alkaline oxides ratios higher than 2 should not present risk of sintering at normal operating combustion temperatures ($850\text{ }^{\circ}\text{C}$) [13]. Indices close to 0.5 were obtained when bales are not subjected to any type of leaching treatment (Figure 7). To reach the recommended index levels to avoid sintering, a minimum immersion time of 5 hours was necessary. As commented in section 3.2, immersion times longer than 1 day did not increase K, Cl, or S leaching and, consequently, index I did not predict any improvement in the ash melting behaviour of the leached biomass either (Figure 7). Therefore, immersion times from 5 hours to 1 day would be the optimal leaching treatment to provide the lowest risk of ash sintering for both types of bales. In addition and, also in accordance with the previous section, index I predicts that water agitation does not favour ash melting behaviour.

It is also worth mentioning that, an index I higher than 2 was obtained for barley straw bales irrigated with 1800 L, in connection with the noticeable K decrease observed when this type of bale was subjected to this leaching treatment.

Figure 7: Earth-alkaline to alkaline oxides ratio (empirical index I) according to the leaching

1 treatment.

2
3 The ash fusibility characteristic temperatures, analysed according to the ISO standard
4 21404:2020, are shown in Table 5 as a function of the leaching treatment. Since hemisphere
5 temperatures (HT) were not always detected, only deformation temperatures (DT) and fluid
6 temperatures (FT) were included in the table.

7
8 **Table 5:** Ash melting characteristic temperatures (according to ISO 21404:2020) according to
9 the leaching treatment.

10
11 DT: deformation temperature; FT: fluid temperature; ND: not determined

12
13
14
15 The DT and FT of immersed samples tended to increase considerably as the immersion time
16 increased, rising from mean DTs of 810 °C (barley) and 900 °C (tall wheatgrass) up to values
17 well above 1150 °C after 1-immersion day. FT also varied extensively with immersion time for
18 the two biofuels tested; from initial mean values around 1100 °C to FTs above 1350 °C after 1
19 immersion day. It is important to note (Table 5) that, once again, water stirring does not seem
20 to affect positively the melting behaviour of tall wheatgrass or barley bales.

21
22 Similarly to the results obtained when applying the predictive index I, water irrigation with 900
23 L did not improve the melting behaviour of tall wheatgrass ashes, and increased very slightly
24 the DT and FT of barley straw ashes (Table 5). In contrast, the irrigation of barley straw bales
25 with 1800 litres of water increased their ash melting temperatures remarkably, up to DT of 1160

1 °C and FT of 1250 °C.

2
3 Therefore, the changes noticed in the ISO 21404:2020 characteristic temperatures with regard
4 to the ash melting behaviour are in close agreement with the predictions obtained by the
5 CIEMAT index I, and with the chemical composition of the biomass before and after bales were
6 leached (section 3.2).

10 **3.4 Effect of leaching on ash corrosion behaviour**

11
12 The reduction of metal thickness under the conditions detailed in section 2.4 (SEM analysis),
13 was used as a measurement of the ash corrosive behaviour of the biomass of tall wheatgrass
14 and barley straw. In this sense, Figure 8 shows the metal corrosion caused by the ashes obtained
15 from the baled biomass before and after the application of the different leaching treatments
16 studied.

17
18
19
20 **Figure 8:** Metal corrosion (SEM analysis) according to the leaching treatment.

21
22 All leaching systems led to a significant improvement on ash corrosion behaviour. Corrosion
23 decreased remarkably with immersion time, from reductions in the metal thickness between 6-
24 7% when bales were not treated until values 3% after bale immersions for 5 h or longer.

1 Irrigating tall wheatgrass bales was not as effective as bale immersion in terms of improving
2 ash corrosion behaviour, probably in connection with the poorest K leaching efficiencies
3 obtained when irrigating this type of bale, as explained in section 3.2. In turn, the irrigation of
4 barley straw bales with 900 and 1800 L proved to be more effective.

5

6 In general, there is a good correlation between the improvements in the ash corrosion (Figure
7 8) and sintering (Figure 7 and Table 4) behaviours with the K content of the baled biomass
8 (Figures 3 and 4). However, K biomass levels (Figures 3 and 4) suggested that the corrosion
9 behaviour of barley straw immersed bales should have been as good as that showed by tall
10 wheatgrass, i.e. the loss of metal thickness in leached bales (Figure 8) of barley straw should
11 have been as low as for tall wheatgrass if we take the similar potassium content into account
12 (Figures 3 and 4). An explanation is that the effect of the biomass ash on corrosion is not directly
13 proportional to contents of inorganic elements such as potassium and many mechanisms,
14 chemical reactions and degree of interactions among the types of the inorganic compounds and
15 the metal interface exist.

16

17 Figure 9 corroborates the above commented difference between barley straw and tall
18 wheatgrass, and shows how the ash/steel interface was reduced when bales were immersed for
19 1 day, for example. When bales were not lixiviated, the resulting corrosion products after
20 heating the ash/steel coupons at 700 °C for 200 h (section 2.4) formed a layer of about 400 µm.
21 The major corrosion product observed in this layer was iron oxide. The thickness of this
22 corrosive layer was reduced from about 400 µm to about 100 µm and 200 µm when tall
23 wheatgrass and barley straw bales were submerged for 1 day, respectively, showing the poorest
24 corrosion reduction of barley.

25

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

Figure 9: Ash/steel interfaces before and after 1-day bale immersions (SEM images).

3.5 Effect of leaching on bale drying

Bale drying is probably the most significant bottleneck to develop leaching systems on a commercial scale, since it can be a considerably long process, which can greatly affect the economic profitability of the entire approach.

In this work, bales were dried indoors under natural ventilation and their moisture content was monitored until reaching values below 20 %. Tall wheatgrass bales dried much faster than barley straw bales, very probably in connection with the lower density of the former. In this sense, the moisture content of tall wheatgrass bales was reduced below 20% (w.b.) after less than 20 days (data not shown). In contrast, more than 100 days were needed for barley straw bales (high-density bales) to reach those moisture levels (Figure 10). Therefore, bale compaction seems to play a very important role when it comes to bale drying.

As can be seen in Figure 10, the drying times for irrigated high-density bales were shorter (between 100 and 120 days) than those needed when bales were submerged during the immersion treatment. This is a consequence of the lower moistures reached by the bales after irrigation (65%) in comparison with those attained after bale immersion (between 70% and 83%, according to immersion time). The type of leaching, either by irrigation or immersion,

1 changes the access of water into the pores or spaces of the straw. The hydrostatic pressure in
2 the immersion process forces water into pores, which cause longer drying times. In contrast,
3 the negligible hydrostatic pressure in the irrigation process reduces the amount of water into
4 the pores decreasing drying times.

5

6

7

8 **Figure 10:** Natural drying of high-density bales after being subjected to different leaching
9 treatments.

10

11 Drying times as long as 140 days were needed to decrease the moisture content of bales, which
12 were previously submerged for 1 hour, below 20%. At the same time, it was clear that the longer
13 the immersion time the longer the drying time. Thus, drying times will be considerably longer
14 than 140 days to reach moistures below 20% in the bales submerged over five hours or more.

15

16

17

18

19

20

21

22

23

1 **4 CONCLUSIONS**

2
3 This work leads to the following conclusions:

4
5 A complete leaching of all the water soluble elements in both high and low density herbaceous
6 bales was reached after water immersions for 24 hours. Nevertheless, bale immersions for 5 h
7 would be enough to reduce the sintering and corrosion of the baled biomass to acceptable levels.

8
9 In the case of high-density bales, the irrigation treatment (1800 L) provided comparable
10 sintering and corrosion reductions to those obtained with the 5 h immersion treatment.
11 However, irrigation was not an effective leaching treatment for low-density bales, probably as
12 a consequence of poorer contact between water and biomass fibers, which resulted in a less
13 efficient lixiviation of alkaline compounds. Therefore, the degree of bale compaction appears
14 to influence the lixiviation process and could be key in selecting the appropriate leaching
15 treatment.

16
17 Furthermore, the leaching studies performed on the two types of herbaceous biomass led to the
18 conclusion that the alkaline compounds present in barley straw, based on potassium chloride,
19 are more readily leached than in tall wheatgrass, which are mainly composed of potassium
20 sulphates. Therefore and, as expected, the water solubility of the different ash forming alkaline
21 compounds affects leaching dynamics.

22
23 The drying time of the lixiviated baled biomass depends on several factors such as bale density
24 or the leaching system applied (immersion or irrigation). The drying time of high-density bales
25 can be considerably long and therefore this aspect should be taken into account when designing

1 industrial processes. Immersion treatments in particular result in elevated biomass moisture
2 contents and therefore longer drying times. Under the conditions tested in this work, more than
3 100 days were necessary to naturally reduce the moisture of this type of bale below 20 wt.%
4 (wet basis). In turn, shorter periods (less than 20 days) were needed to reach the same moisture
5 levels when drying low-density bales.

6

7

8

9

10

5 REFERENCES

- [1] De Laporte AV, Weersink AJ, McKenney DW. Effects of supply chain structure and biomass prices on bioenergy feedstock supply. *Applied Energy* 2016;183:1053–64. <https://doi.org/10.1016/j.apenergy.2016.09.049>.
- [2] Jenkins BM, Bakker RR, Wei JB. On the properties of washed straw, *Biomass and Bioenergy* 1996;10:177-200. [https://doi.org/10.1016/0961-9534\(95\)00058-5](https://doi.org/10.1016/0961-9534(95)00058-5).
- [3] Allica JH, Mitre AJ, Bustamante JA, Itoiz C, Blanco F, Alkorta I, Garbisu C. Straw quality for its combustion in a straw-fired power plant. *Biomass and Bioenergy* 2001;21,249-58.
- [4] Yu C, Thy P, Wanga L, Anderson SN, VanderGheynst JS, Upadhyaya SK, Jenkins BM. Influence of leaching pretreatment on fuel properties of biomass. *Fuel Processing Technology* 2014;128:43–53. <https://doi.org/10.1016/j.fuproc.2014.06.030>.
- [5] Niu Y, Tan H, Hui S. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. *Combustion of agricultural residues. Progress in Energy and Combustion Science* 2016;52:1-61. <https://doi.org/10.1016/j.peccs.2015.09.003>.
- [6] Miles TR-Jr, Miles TR. Alkali deposits found in biomass power plants. Summary report for National Renewable Energy Laboratory. NREL Subcontract TZ-2-11226-1, 1994.
- [7] Werther J, Saenger M, Hartge E-U, Ogada T, Siagi Z. Combustion of agricultural residues. *Progress in Energy and Combustion Science* 2000;26:1-27. [https://doi.org/10.1016/S0360-1285\(99\)00005-2](https://doi.org/10.1016/S0360-1285(99)00005-2).
- [8] Fernández-Llorente MJ, Escalada-Cuadrado R, Murillo-Laplaza JM, Carrasco-García JE. Combustion in bubbling fluidised bed with bed material of limestone to reduce the biomass

1 ash agglomeration and sintering. Fuel 2006;85:2081-92.

2 <https://doi.org/10.1016/j.fuel.2006.03.018>.

3 [9] Bakker RR, Jenkins BM. Feasibility of collecting naturally leached rice straw for thermal
4 conversion. Biomass and Bioenergy 2003;25:597-614. [https://doi.org/10.1016/S0961-](https://doi.org/10.1016/S0961-9534(03)00053-9)
5 [9534\(03\)00053-9](https://doi.org/10.1016/S0961-9534(03)00053-9).

6 [10] Jensen PA, Sander B, Dam-Johansen K. Pretreatment of straw for power production by
7 pyrolysis and char wash. Biomass and Bioenergy 2001;20:431-46.
8 [https://doi.org/10.1016/S0961-9534\(01\)00005-8](https://doi.org/10.1016/S0961-9534(01)00005-8).

9 [11] CENNATEK BIOANALYTICAL SERVICES. Feasibility of Improving Biomass
10 Combustion through Extraction of Nutrients, 2011. [https://ofa.on.ca/wp-](https://ofa.on.ca/wp-content/uploads/2017/11/Improving_Biomass_Combustion_-_nutrient_Extraction-2_RAAC.pdf)
11 [content/uploads/2017/11/Improving_Biomass_Combustion_-_nutrient_Extraction-2_RAAC.pdf](https://ofa.on.ca/wp-content/uploads/2017/11/Improving_Biomass_Combustion_-_nutrient_Extraction-2_RAAC.pdf).

12 [12] CEN/TS 15370-1:2006, Solid Biofuels — Determination of ash melting behaviour – Part
13 1: Characteristic temperatures method. CEN European Committee for Standardization.

14 [13] Fernández-Llorente MJ, Carrasco-García JE, Comparing methods for predicting the
15 sintering of biomass ash in combustion, Fuel 2005;84:1893-1900.
16 <https://doi.org/10.1016/j.fuel.2005.04.010>

17

18

Table 1: Bale characteristics

	Tall wheatgrass	Barley straw
Weight (kg)	14	30
Size (cm)	100×38×46	125×50×35
Surface (m ²)	0.46	0.75
Volume (m ³)	0.17	0.22
Density (kg/m ³)	80	137

Table 2: Leaching treatments

	1 hour
Immersion (into 900 litres)	1 hour + stirring
	5 hours
	24 hours
	48 hours
Irrigation	900 litres (3 hours)
	1800 litres (6 hours)

Table 3: Standards and analytical methods

Property	Analytical technique	Standard
Sample preparation	Homogenisation, subsampling, milling	ISO 14780:2017
Moisture	Drying at 105 °C	ISO 18134-2:2017
Ash	Calcination at 550 °C	ISO 18122:2015
C, H, N	Elemental analysis: IR and TCD (Leco, TruSpec)	ISO 16948:2015
S and Cl	Combustion bomb (Ika) + IC (Methrom)	ISO 16994:2016
Calorific value	Calorimetry (Ika, C5000)	ISO 18125:2017
Major-minor elements	MW digestion + ICP-OES (Thermo Fisher, Iris AP)	ISO 16967:2015
Inorganic compounds	X-ray diffraction (PANalytical, X'pert-PRO)	ISO 16968:2015
Ash melting behaviour	Optical heating microscopy (Hesse)	ISO 21404:2020

Table 4: Characterisation of the barley and tall wheatgrass baled biomass.

Unit		Tall wheatgrass (n=6)			Barley straw (n=7)		
		<i>Mean</i>	<i>sd</i>	<i>%<i>rsd</i></i>	<i>Mean</i>	<i>sd</i>	<i>%<i>rsd</i></i>
<i>Calorific values</i>							
GCV	MJ/kg d.b.	18.78	0.08	0.45	17.53	0.29	1.7
NCV	MJ/kg d.b.	17.44	0.08	0.44	16.25	0.3	1.8
<i>Proximate analysis</i>							
Ash	wt.% d.b.	4.3	0.4	8.6	7.1	0.4	5.8
<i>Ultimate analysis</i>							
Carbon	wt.% d.b.	44.6	0.4	8.6	44.3	0.6	1.4
Hydrogen	wt.% d.b.	6.1	0.05	0.84	5.9	0.1	1.3
Nitrogen	wt.% d.b.	1.0	0.2	19	0.42	0.09	21
Sulphur	wt.% d.b.	0.10	0.03	27	0.06	0.01	18
Chlorine	wt.% d.b.	0.18	0.07	41	0.62	0.15	25
<i>Ash composition on ash 550 °C</i>							
Al ₂ O ₃	wt.% d.b.	1.6	0.4	24	0.48	0.38	78
CaO	wt.% d.b.	9.0	0.5	5.7	7.8	0.7	8.5
Fe ₂ O ₃	wt.% d.b.	0.53	0.08	15	0.19	0.1	54
K ₂ O	wt.% d.b.	23	3.0	13	21	1.6	7.5
MgO	wt.% d.b.	3.0	0.6	20	2.9	0.1	4.0
Na ₂ O	wt.% d.b.	0.47	0.11	22	2.2	0.6	29
P ₂ O ₅	wt.% d.b.	5.4	0.8	14	1.3	0.1	5.4
SO ₃	wt.% d.b.	5.8	1.0	14	2.7	0.2	8.9
SiO ₂	wt.% d.b.	38	5.9	16	43	2.0	4.6
TiO ₂	wt.% d.b.	0.057	0.045	83	0.023	0.02	84
ZnO	wt.% d.b.	0.084	0.037	43	0.010	0.003	27
Sum		86.3			86.5		
<i>Fusibility temperatures</i>							
Deformation	°C	900	73	8.2	810	22	2.8
Hemisphere	°C	1090	33	3	1030	18	1.7
Fluid	°C	1170	57	4.9	1090	16	1.5

d.b.: dry basis; GCV: gross calorific value at constant volume; NCV: net calorific value at constant pressure; ND: not determined

Table 5: Ash melting characteristic temperatures (according to ISO 21404:2020) depending on the leaching treatment.

Leaching treatment	Tall wheatgrass		Barley straw	
	DT	FT	DT	FT
Initial	900	1170	810	1090
1 hour	950	1280	940	1260
Immersion 1 hour+ stirring	910	1140	880	1240
5 hours	1070	1300	1120	1280
1 day	1160	1360	1220	1400
2 days	1320	> 1450	1280	> 1450
Irrigation 900 L	830	1150	870	1150
1800 L	ND	ND	1160	1250

DT: deformation temperature; FT: fluid temperature; ND: not determined

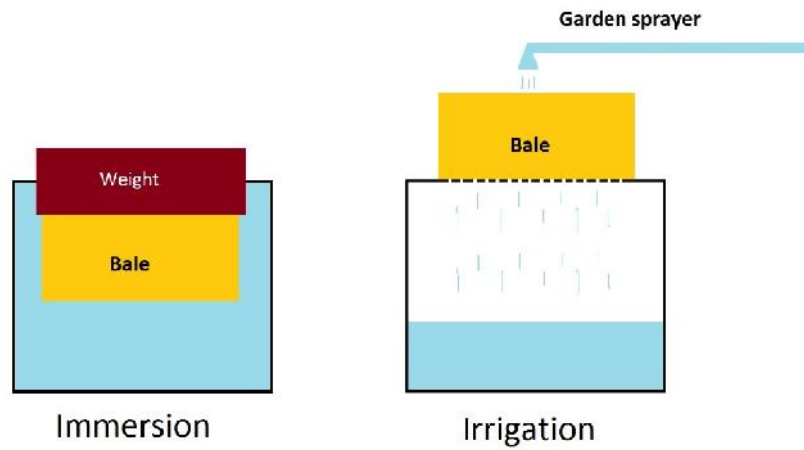


Figure 1: Scheme of the two different bale leaching treatments

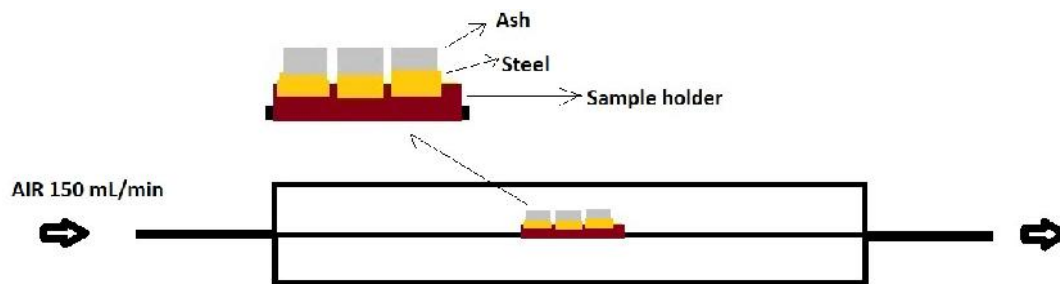


Figure 2: Schematics of the corrosion test using a tubular furnace.

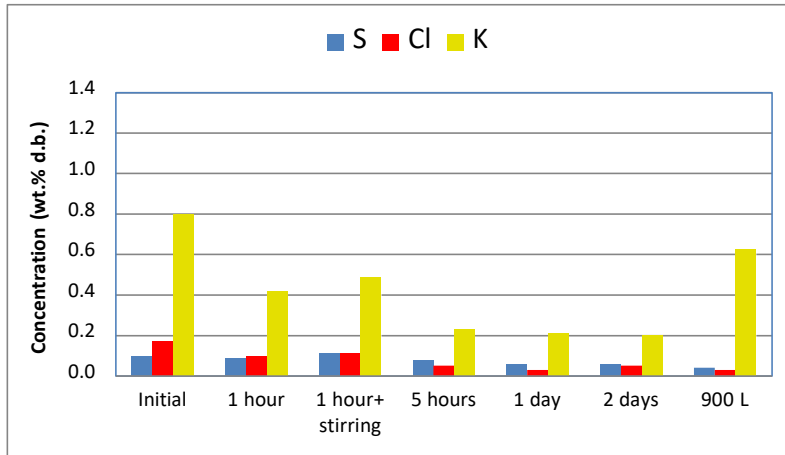


Figure 3: S, Cl, and K concentrations on the baled tall wheatgrass biomass depending on the leaching treatment.

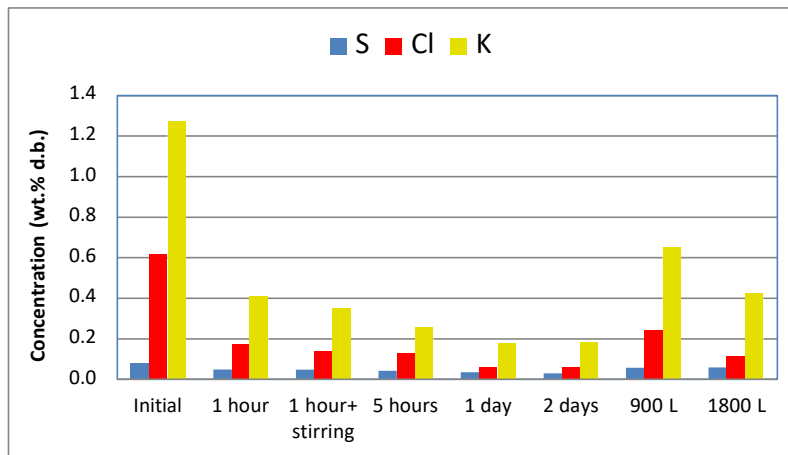


Figure 4: S, Cl, and K concentrations on the baled barley straw biomass depending on the leaching treatment.

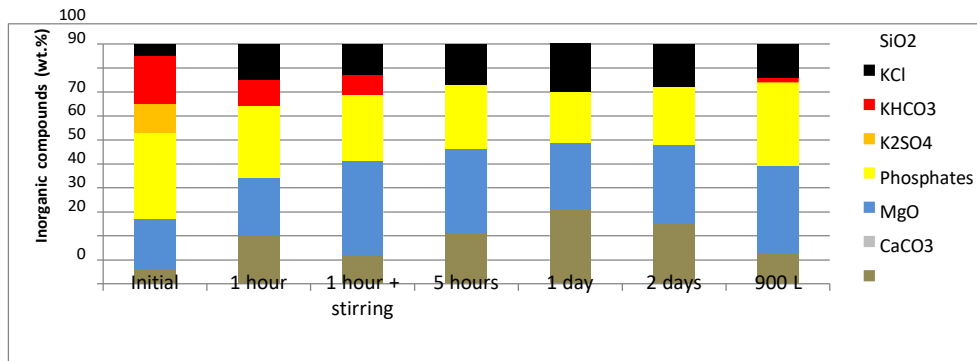


Figure 5: Ash inorganic compounds of tall wheatgrass bales depending on the leaching treatment (XRD analysis)

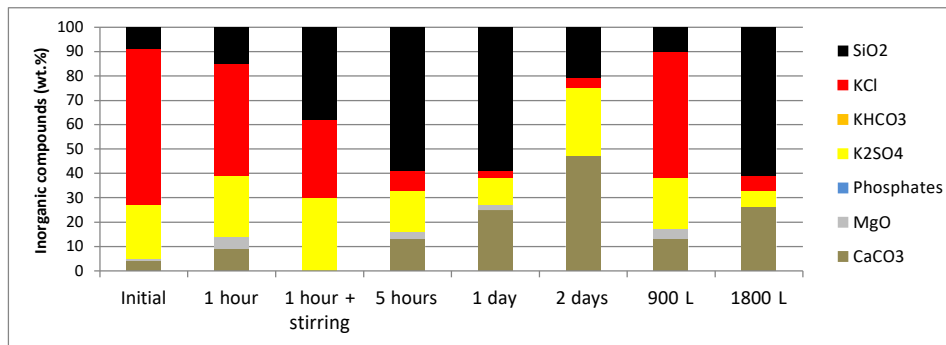


Figure 6: Ash inorganic compounds of barley straw bales depending on the leaching treatment (XRD analysis)

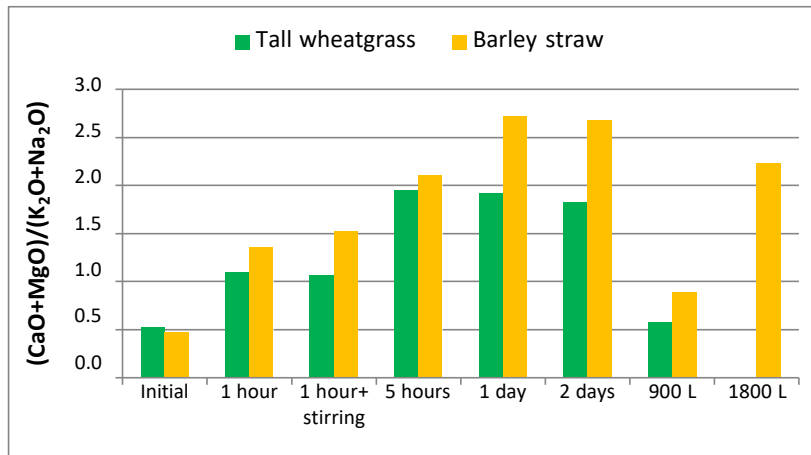


Figure 7: Earth-alkaline to alkaline oxides ratio (empirical index I) depending on the leaching treatment.

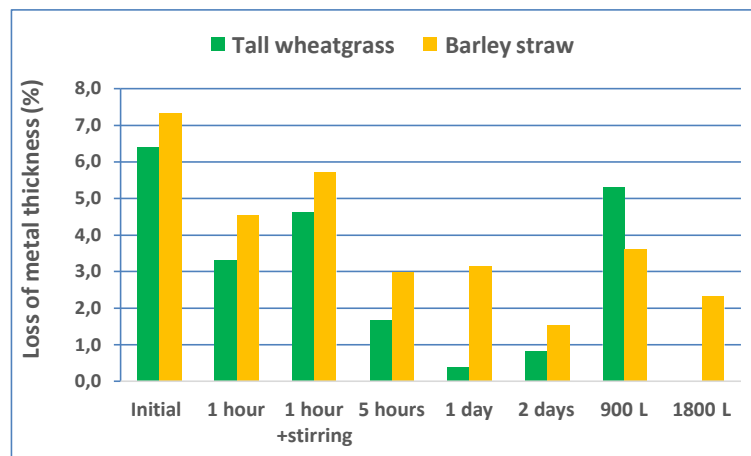


Figure 8: Metal corrosion (SEM analysis) depending on the leaching treatment.

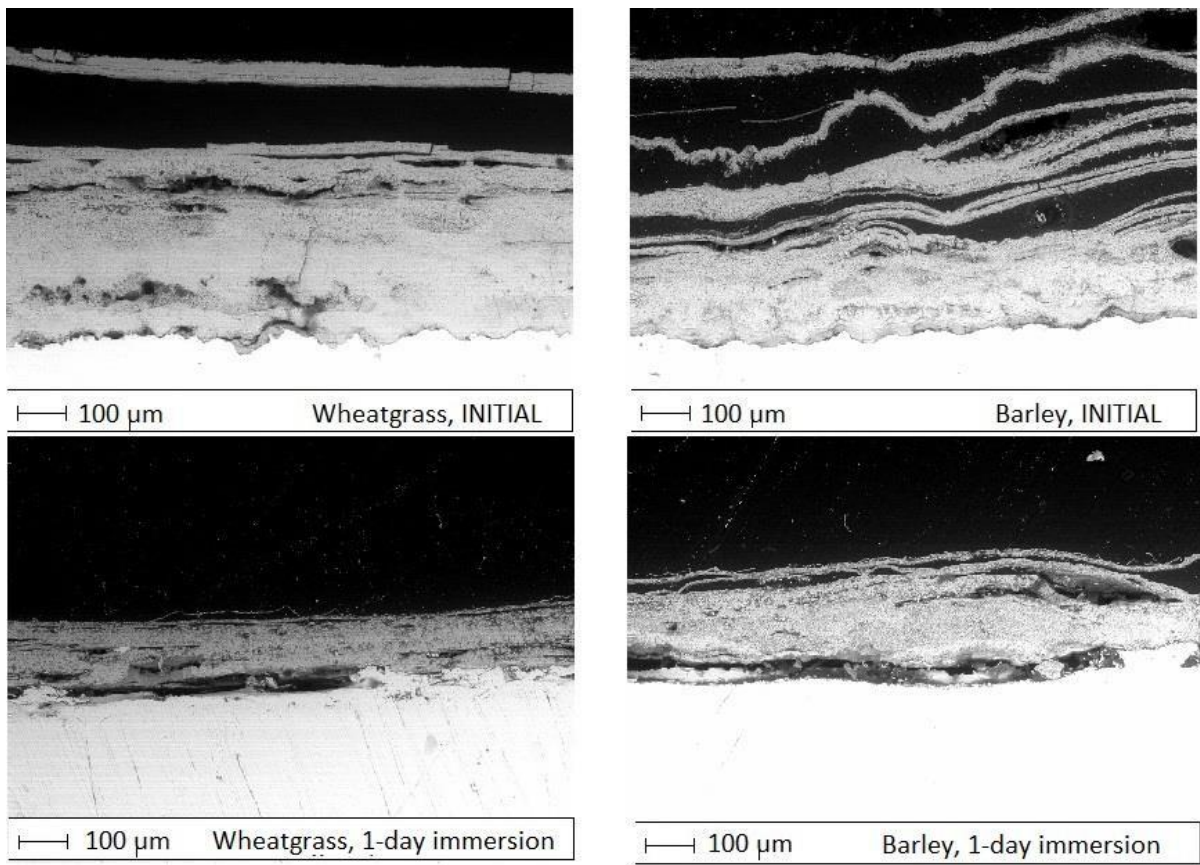


Figure 9: Ash/steel interfaces before and after 1-day bale immersions (SEM images).

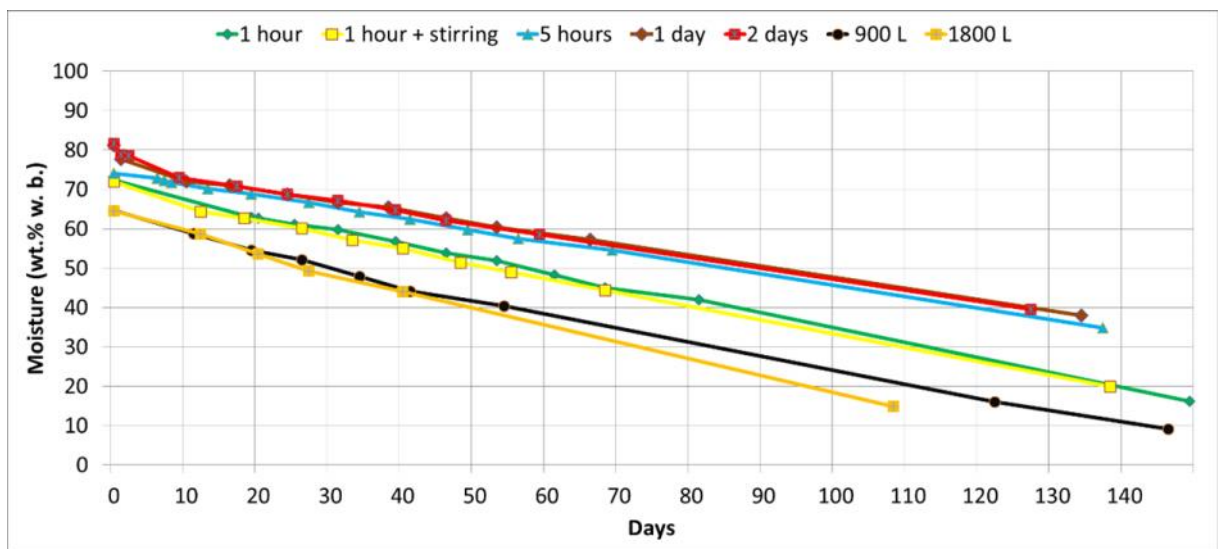


Figure 10: High-density bales natural drying after being subjected to different leaching treatments.

