



# Improving inorganic composition and ash fusion behavior of spruce bark by leaching with water, acetic acid, and steam pre-treatment condensate

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## ABSTRACT

The present study evaluates the effect of water and acetic acid washing on the chemical composition of spruce bark in-depth. Also, washing with steam explosion condensate (SEC) was investigated which is a novel attempt. The leaching kinetics of troubling elements (TE) was studied to understand the leaching behavior of TEs and for upscaling the process. Furthermore, to study the ash transformation behavior of TEs in pre-treated and raw bark at high temperatures (500–1500 °C), thermodynamic equilibrium modeling (TEM) was also performed. The result of washing pre-treatment shows high removal of TEs: 22–97% Na, 46–82% Cl, 14–79% K, 14–65% Mg, 25–50% S, 3–22% Ca, 12–36% P, 3–43% Si, and 6–35% N. Continuous removal of TEs was seen with increasing washing duration where most of TEs followed a second-order leaching kinetics. Acid washing results in a much higher and quicker removal for all TEs than water washing. Due to the acidic nature of the SEC, it shows similar removal of TEs as the 0.1 M acetic acid solution. TEM reveals that the transformation behavior of TEs in bark changes considerably after pre-treatment. Pre-treated bark shows the formation of fewer problematic compounds responsible for fouling, slagging, and corrosion at typical gasification and combustion temperatures, such as KCl, K<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, KOH, Na<sub>2</sub>SO<sub>4</sub>, NaCl, and K-, Na-, P-, and Ca-slag. Though best washing efficiency was seen for longer washing durations, 10 min washing with 0.1 M acetic acid or SEC may be adequate for practical applications.

## 1. Introduction

In the fight against climate change, lignocellulosic biomass residues are one of our strongest allies because of their ample availability and carbon neutrality. To reduce their carbon footprint, countries such as Finland, Sweden, Norway, Canada, Austria, Germany, USA, UK, and China are now actively increasing the share of bioenergy in their energy mix [1]. Subsequently, the concept of biorefinery is becoming more common worldwide and the market for new & upgraded solid biomass fuels (pellets and briquettes) is increasing rapidly. Gradually, interest in low-grade biomass residues with high ash content is growing because of the high demand for white pellets and limited availability of forest wood and wood residues. One such biomass with a high energy and chemical recovery potential is bark.

Food and Agriculture Organization estimated that globally around 400 million m<sup>3</sup> of bark is produced annually [2]. Despite its abundance, most bark is left in the forest or used as low-grade fuel for heat and energy in local communities and industries. One of the reasons behind its limited utilization in thermochemical applications like combustion, pyrolysis, and gasification, is the high content of ash and TE such as K, Na, Cl, S, N, Si, and P [3,4]. In general bark from beech, elm, eucalyptus, maple, pine, spruce, and tamarack has high ash content (>2%) [5–9]. These barks typically contain about 2–8% ash, 0.1–0.5% K, 0–0.3% Cl, 0–0.2% Na, 0.1–0.7% N, and 0–0.1% S [3,9,10], which are higher than the permissible values of many pellet standards [11–13]. The high content of K and Na, together with Cl and S, can lead to issues such as fouling of heat exchangers, fireside deposits, high- and low-temperature corrosion, agglomeration of fluidized bed, and ash fusion in gasification

**Abbreviations:** AI, Alkali index; AAEM, Alkali and alkaline earth metals; COD, Chemical oxygen demand; HHV, High heating value; HPLC, High-performance liquid chromatography; RO, Reverse osmosis; SE, Steam explosion; SEC, Steam explosion condensate; TE, Troubling inorganic elements; TEM, Thermodynamic equilibrium modeling; TOC, Total organic carbon; XRF, X-ray fluorescence.

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and combustion boilers [14–18]. During pyrolysis, AAEM lead to bio-oil cracking and promote the formation of char and gaseous products over bio-oil [19–22]. In biomass gasification, Si present in biomass inhibits the catalytic effect of K and deactivates the effect of Ni and Fe catalyst, reducing quality of the generated syngas [23,24]. As the TEs hinder thermochemical conversion, pre-treatment of bark is essential.

Washing or leaching pre-treatment is a simple and effective way to reduce the content of TEs from high ash-containing biomass feedstock. Due to its operational simplicity and low capital costs, washing is becoming more attractive for large-scale industrial applications and researchers [25]. Just in the year 2022, several studies have been published on washing pre-treatment using different types of feedstock such as straw [26–28], aquatic biomass [29], grasses [28], and stalk [30]. These studies show that >90% of K, Cl, Na, and about 10–70% Ca, Mg, P, and Si can be removed by water washing. As a result, better yield and quality of bio-oil and syngas were noted in pyrolysis and gasification [21,22,30–32]. Even though there is a high research interest in washing, studies published on the washing pre-treatment of bark and other forest residues are very limited. To best of our knowledge, only one study by Liu and Bi (2011) [23] was found on bark washing treatment, where <10% removal of ash upon water washing, and 36–54% removal upon acid washing was reported from pine bark. About 30–36% K and Na, 55–88% Ca, Mg, Fe, and P, and 25–30% Si and S in bark can only be leached out using a buffer and acid solutions [3,5]. So, to remove organically associated and water-insoluble salts of K, Na, Cl, Ca, Mg, Si, Fe, and P, several researchers have used various strong acids such as HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> to remove these TEs from biomass [33–35]. However, after acid-washing, the treated material must be neutralized to avoid corrosion and SO<sub>x</sub>, NO<sub>x</sub>, and HCl emissions in thermochemical applications. This neutralization step requires high amounts of water and other chemicals, which are an economic and environmental burden for industries [21]. Also, washing with strong acids can hydrolyze the hemicellulose and cellulose into smaller molecules which may be undesirable for pyrolysis and fermentation applications [23]. As washing with diluted acetic acid can solve the emission and leaching efficiency issue, it is more attractive for practical applications. Though buying high amounts of acids for large-scale applications may not be economically and environmentally sustainable in the long run. For that reason, industrial waste streams rich in organic acids are the ideal solvent for leaching pre-treatment purposes such as steam explosion condensate.

Steam explosion or autohydrolysis has been extensively explored over the past few decades to improve lignocellulosic biomass quality for second-generation bioethanol production. One of the by-products SE plants is steam released together with volatile organic compounds (VOC) after the treatment, which is collected afterwards as liquid called SEC. As most VOCs released during the SE of lignocellulose are organic acids and furfural, the pH of the condensate can be highly acidic (<3) depending on the severity of the treatment [36,37]. Because of its high acidity and availability in large-scale SE plants, SEC may be an interesting solvent for leaching pre-treatment. Presently, the detailed composition of SEC from bark feedstock is missing in the available literature, making it further interesting to study and chemical recovery.

Advanced multicomponent and multiphase thermodynamic equilibrium modeling can be a powerful tool for predicting different ash-related challenges in different thermochemical technologies. TEM is widely used by several researchers for studying ash deposition behavior [38–40], bed agglomeration [41], and aerosol formation [42] for a wide range of biomasses such as wood, bark, shells, husk, straw, and grasses [43]. Several researchers also used TEM to compare ash fusion and melting behavior of different types of biomasses. For example, Link et al. [39] used TEM to compare the ash melting behavior of reeds and wheat straw, while others reported [42] its use for evaluating different agricultural residues, and wood fuel blends. To the best of our knowledge, TEM has not been used to study ash behavior for pre-treated and untreated biomass. Also, the abovementioned studies show that water and acid washing effectively reduce ash and TE-content from biomass.

However, most of these studies are limited to 2–3 washing data points and are insufficient for identifying conclusive trends in the leaching behavior. Further, no detailed study on the spruce bark pretreatment through water or acid washing or the leaching kinetics has been published.

The aim of the present study is to evaluate the impact of washing pre-treatment on the inorganic composition and ash fusion behavior of spruce bark in-depth. Effect of washing with water, acetic acid and SEC was studied thoroughly to understand the leaching behavior of different TEs. Leaching kinetics of different TEs were also studied in detail as it is crucial for upscaling and understanding the overall process. Then, TEM was used to study the transformation of critical ash-forming elements in the raw and pretreated bark at high temperatures (500–1500 °C). The detailed effects of leaching duration were evaluated by varying the washing time from 0 min (i.e., quick spraying) to 180 min for both water and acid washing experiments. A total of 21 washing experiments were conducted, which were analyzed later in detail to study the change in biomass composition, calorific value, mass and energy losses, and fouling and slagging propensity.

## 2. Materials and methods

The Norway spruce (*Picea abies*) bark samples were collected from the debarking unit at Koski TL, Finland. Samples were collected immediately after dry debarking the moist log in two different batches (Figure S1). The first batch was used for water leaching experiments (performed in February 2022), while bark from the second batch was used for acetic acid and SEC washing experiments (performed in April 2022). Originally bark samples contained about 52–55% moisture which was dried overnight (at 104 ± 2 °C) and the sample was ground to pass through the sieve size 5 mm. The ground samples were then sealed and store in an airtight container for washing experiments.

### 2.1. Washing experiments

Three different types of washing experiments were conducted in the present study – washing with water, 0.1 M acetic acid and SEC (Fig. 1). The 0.1 M acetic acid solution (pH 2.87) was used to simulate the SEC (pH 2.85) because only a limited amount of SEC was available for use. This was justified because the major component of SEC was acetic acid (as shown in Table S3) and pH of both the solution was comparable. SE tests with spruce bark were conducted at Lund University in a preheated reactor at 220 °C with a residence time of 5 min to obtain the SEC used. Figure S10 shows the schematics of the SE reactor, and detailed information regarding its design and operation are included in Böch et al. [44]. It should be noted that due to the reactor limitations, all the condensate generated could not be collected.

In each washing experiment, 10 g of bark was washed with 150 ml of respective solution. For water and acetic acid washing, 8 batch washing experiments were conducted of duration – 0 min, 2 min, 5 min, 10 min, 15 min, 30 min, 60 min, and 180 min. One sample for each water and acid washing was tested and named “0 min” to study the effect of quick spraying on spruce bark. For the 0 min washing, 150 ml of solution was poured over the sample within just 5–8 s, and the leachate was simultaneously removed from the bottom. The experimentally obtained SEC was used for 180 min washing experiment to compare the results. The pH and electrical conductivity of the leachate samples were measured after washing experiments.

For error analysis, the 10 min water- and acid-washing experiment were repeated thrice as short washing duration experiments show higher fluctuations in removal [45]. In comparison, the SEC washing experiment was repeated only twice due to limited availability. The maximum error in the removal efficiency observed was < 3% (Figure S2). After washing and filtration, wet solid samples were dried overnight at 104 ± 2 °C and then left to absorb moisture at room temperature for 24 h [25,46,47]. Afterward, the samples were stored in airtight containers

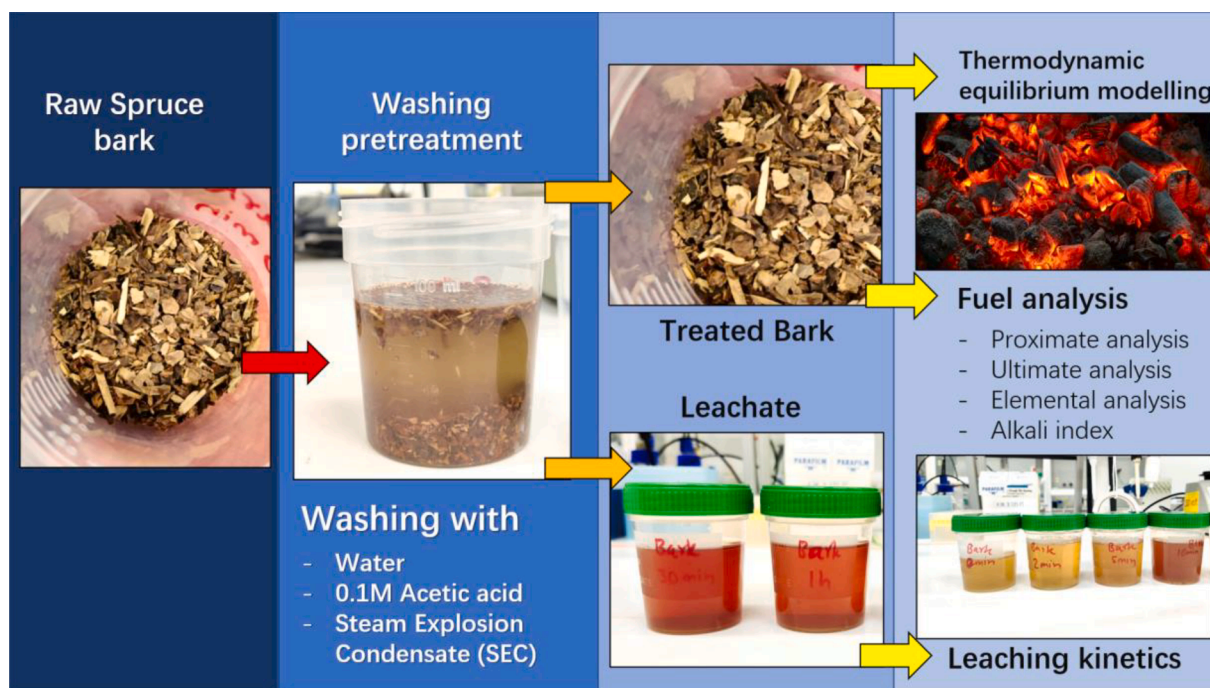


Fig. 1. Experimental flow diagram of the present study.

and used for further analysis.

## 2.2. Analytical methods

The composition of all the washed samples were analyzed using proximate, ultimate, and XRF analysis. The HHV of all samples was calculated from the elemental analysis. The methods for determining the compositions, HHV and AI of solid fuel are mentioned in Table 1. All measurements were made in triplicate.

Mass and energy yield in individual washing case were calculated by using the formulas [45]:

$$\text{Mass yield} = \left( \frac{M_w}{M_o} \right) \times 100\% \quad (1)$$

$$\text{Energy yield} = \left( \frac{\text{HHV}'_{ar,mf} \times m_w}{\text{HHV}_{ar,mf} \times m_o} \right) \times 100\% \quad (2)$$

where  $M_w$  and  $M_o$  are the weight of the sample after and before leaching, while  $\text{HHV}'_{ar,mf}$  and  $\text{HHV}_{ar,mf}$  are the HHV of the leached and original sample calculated on the as-received and moisture-free basis.

**Table 1**  
Analytical methods used in the present study.

| Analysis                      | Instrument used                                    | Method/formula used  | Reference |
|-------------------------------|--|--|-----------|
| Proximate Analysis            | Heating oven and Muffle furnace                    | ASTM E872 – 82 (2006) and ASTM E1755 – 01 (2007)                         | –         |
| Ultimate Analysis (dry basis) | Thermo Scientific™ Flash Smart™ Elemental Analyzer | BS EN 15104:2011   | –         |
| High-Heating value (HHV)      | Thermo Scientific™ Flash Smart™ Elemental Analyzer | HHV (MJ/kg) = 0.3491C + 1.1783H + 0.1005S – 0.1034O – 0.0151 N – 0.0211A | [48]      |
| Inorganic composition of ash  | Thermo Scientific™ Niton XL3t GOLDD+               | X-ray fluorescence (XRF)   | –         |
| Fouling prediction            | –  | AI = $F_{\text{ash}} (F_{K2O} + F_{Na2O}) / \text{HHV}$                  | [34]      |

To calculate the removal efficiency of various elements, the relation provided by [25] was used:

$$X_i \left( 1 - \frac{m_w \times R_w}{m_o \times R_o} \right) \times 100\%, \quad (3)$$

where  $X$  is the removal efficiency,  $i$  represents the removed element or constituent, and  $R_w$  and  $R_o$  are the mass fraction of the respective constituents in the washed and original sample.

The AI of raw and pre-treated bark was used to predict the fouling and slagging propensity. The formula used for calculating AI was:

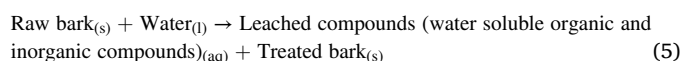
$$\text{Alkali index (AI)} = F_{\text{ash}} \frac{(F_{K2O} + F_{Na2O})}{\text{HHV}} \quad (4)$$

here,  $F_{\text{ash}}$  is the mass fraction of the ash in the bark (on a dry basis), HHVs are expressed in GJ/kg, and  $F_{K2O}$  and  $F_{Na2O}$  are the mass fractions of  $K_2O$  and  $Na_2O$  in the ash.  $AI < 0.17$  implies probable fouling, while  $AI > 0.34$  implies fouling will occur [34].

HPLC was used to measure the content of organic acids (acetic acid, levulinic acid, and formic acid) and furfural present in the SEC. A Shimadzu Scientific HPLC Instrument (Kyoto, Japan) was used for the measurement. It was equipped with a refractive index detector (RID-10A; Shimadzu Scientific Instruments), LC-20AT pump, DGU-20A3 degasser, SIL-20AC autosampler, and CTO-20AC column oven. The Column used for detection was the Aminex HPX87H column (Bio-Rad Laboratories, Hercules, USA) at 50 °C, 0.5 ml/min, with 0.005 M  $H_2SO_4$  as the eluent.

## 2.3. Leaching kinetics

The leaching kinetics of TEs and ash were examined in the present study with respect to leaching duration of water and acid-washing. The data fitting method with experimental results was used in second-order kinetic models to evaluate the leaching rate and study the leaching behavior of different TEs. The leaching process was assumed to proceed as:



The leaching of inorganic species was assumed irreversible for the present study [49,50]. The differential equations used for second-order kinetics to study the leaching of different elements are as follows:

$$\frac{dC_t}{dt} = k(C_s - C_t)^2 \quad (6)$$

where  $k$  is the leaching rate constant,  $C_s$  is the saturated concentration (g/L) of the respective element in the leachate, and  $C_t$  is the concentration of the respective element in the leachate at time  $t$  (in min). The integration of the differential equation after applying boundary conditions [ $C_t$  (at  $t = 0$  min) to  $C_t = C_t$  (at  $t = t$  min)] gives:

$$C_t = \frac{ktC_s^2}{1 + ktC_s} \quad (7)$$

#### 2.4. Thermodynamic equilibrium modeling

TEM was performed to predict the equilibrium phases formed during the ash transformation process. TEM calculations are based on Gibbs free energy minimization principle. During the calculations, kinetic limitations were not considered. The methodology used in the present study was based on Link et al. [39,40], where they have also validated the modeling result with experimental findings. The calculations were performed using the Equilib module of Factsage 8.1 software. The following databases were considered for the calculations: FactPS, FToxid (SLAGA and Bred), and FTSalt (SALTF, B1, op28D, hP22, and hP14). The equilibrium calculations were performed for 100 kg of samples as input. Sample studied were raw bark, water-washed bark for 10 and 180 mins, and acid-washed bark for 10 and 180 mins. The input values were based on the biomass analysis shown in Table 2. For calculations, the pressure was kept constant at 1 bar while the temperature was varied between 500 °C and 1500 °C with a step of 100 °C.

Furthermore, oxidizing gas atmosphere was considered with an actual to theoretical air input ratio of 1.15. While modeling, it was assumed that all the participating components were distributed in a thoroughly mixed steady-state condition with uniform temperature and infinite residence time. However, that may not be true in the actual case-scenario due to which the TEM results do not always necessarily represent actual scenarios [38,40,43]. Therefore, TEM results should be considered for qualitatively understanding the transformation behavior of critical ash elements of the considered feedstocks.

**Table 2**  
Data input for Factsage software in grams (Sample considered 100 kg).

| Elements       | Raw bark  | 10 min ww | 180 min ww | 10 min aw | 180 min aw | SEC wash  |
|----------------|-----------|-----------|------------|-----------|------------|-----------|
| C              | 48625.00  | 48075.00  | 47734.13   | 48584.89  | 49413.19   | 49002.00  |
| H              | 5659.54   | 5655.42   | 5616.85    | 5447.81   | 5756.02    | 5740.00   |
| N              | 250.00    | 230.00    | 238.00     | 246.00    | 244.00     | 224.00    |
| O              | 42001.05  | 42898.72  | 43320.24   | 43646.60  | 42788.55   | 43007.76  |
| K              | 397.62    | 225.43    | 185.38     | 129.34    | 68.27      | 81.19     |
| Cl             | 8.06      | 2.98      | 2.23       | 1.72      | 1.33       | 1.11      |
| S              | 34.81     | 25.64     | 25.04      | 17.48     | 16.13      | 16.69     |
| Ca             | 1043.20   | 1041.56   | 1070.55    | 781.33    | 780.05     | 712.40    |
| Si             | 27.36     | 26.81     | 27.18      | 20.37     | 18.29      | 20.84     |
| Mg             | 143.43    | 109.40    | 81.44      | 64.28     | 51.03      | 45.77     |
| P              | 82.56     | 75.30     | 74.00      | 51.00     | 45.59      | 50.00     |
| Fe             | 34.42     | 16.03     | 16.64      | 15.66     | 16.30      | 21.78     |
| Na             | 113.53    | 25.38     | 18.88      | 14.98     | 8.58       | 3.20      |
| Al             | 40.12     | 37.05     | 36.40      | 23.49     | 19.46      | 26.27     |
| Ti             | 0.00      | 0.00      | 0.00       | 0.00      | 0.27       | 0.22      |
| Zn             | 47.69     | 45.45     | 43.73      | 27.54     | 25.87      | 29.32     |
| Cu             | 0.90      | 0.55      | 0.52       | 0.43      | 0.55       | 0.69      |
| Ni             | 1.01      | 0.49      | 0.71       | 0.31      | 0.47       | 0.66      |
| Mn             | 120.78    | 129.00    | 119.57     | 64.04     | 59.04      | 57.17     |
| Cr             | 0.97      | 0.42      | 0.67       | 0.35      | 0.38       | 0.51      |
| O <sub>2</sub> | 149116.67 | 147430.00 | 146384.67  | 148993.68 | 151533.79  | 150272.80 |
| N <sub>2</sub> | 447350.00 | 442290.00 | 439154.02  | 446981.03 | 454601.37  | 450818.40 |

### 3. Result and discussion

#### 3.1. Effect of washing on ash, C, H, and O content, HHV, mass, and energy yields

After pretreatment, the elemental composition of bark was studied thoroughly in the present study; results are shown in Fig. 2 and Table 3. From the results, it was evident that leaching pre-treatment has a high impact on the elemental composition of bark. Continuous removal of inorganics was noted in both water and acid-washing with increasing leaching duration. As a result, the ash content of the bark shows a continuous removal (Fig. 2). Until 10 min, the ash removal and increment in volatile content were rapid. Even on quickly rinsing with water (0 min), about 11% ash removal was seen. As acid-washing partially breaks the biomass structure, the increment in volatile content seen in acid and condensate washing was much higher than in water washing experiments. After 10 min, it was relatively slower, especially for longer durations (>60 min) though still significant. As no detailed studies were available on bark washing, the results cannot be compared with other studies. However, similar trends were seen in other washing studies published on wheat straw [51], empty fruit bunches or EFB [45], rice husk [52], and mallee leaves [53]. The main reason behind reduction in the ash content was the removal of extraneous impurities (grit, soil, dirt) and water-soluble inorganic species (NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>+2</sup>, Ca<sup>+2</sup>, K<sup>+</sup>, Na<sup>+</sup>). The ash removal efficiency observed in water-washing was not very high (<20%) because of the high content of water-insoluble compounds of Ca, Mg, Si, and P in the bark. They exist in spruce bark in high amounts (Table S2), which are either covalently bonded to the organic matrix or present as water-insoluble compounds such as Ca- and Mg-oxalates, carbonates, phosphates, silicates [3,5]. However, most of these compounds are leachable with an acid. As a result, 15–43% removal of ash was noted in acetic and condensate washing experiments.

After washing, a slight reduction in C and H was noted (<1%). On the contrary, O content after water-washing increases slightly. The slight reduction in C and H could result from the leaching of some organic compounds such as sugars, organic acids, esters, and phenols, which are reported for bark in some water extraction studies [7,54,55]. Consequently, some mass loss is inevitable in the leaching pre-treatment, as seen in the present study and some past studies on other biomasses [25,56]. After water-washing, HHV of the treated bark reduced slightly (<0.5 MJ/kg). While after acid-washing, it fluctuated but remained

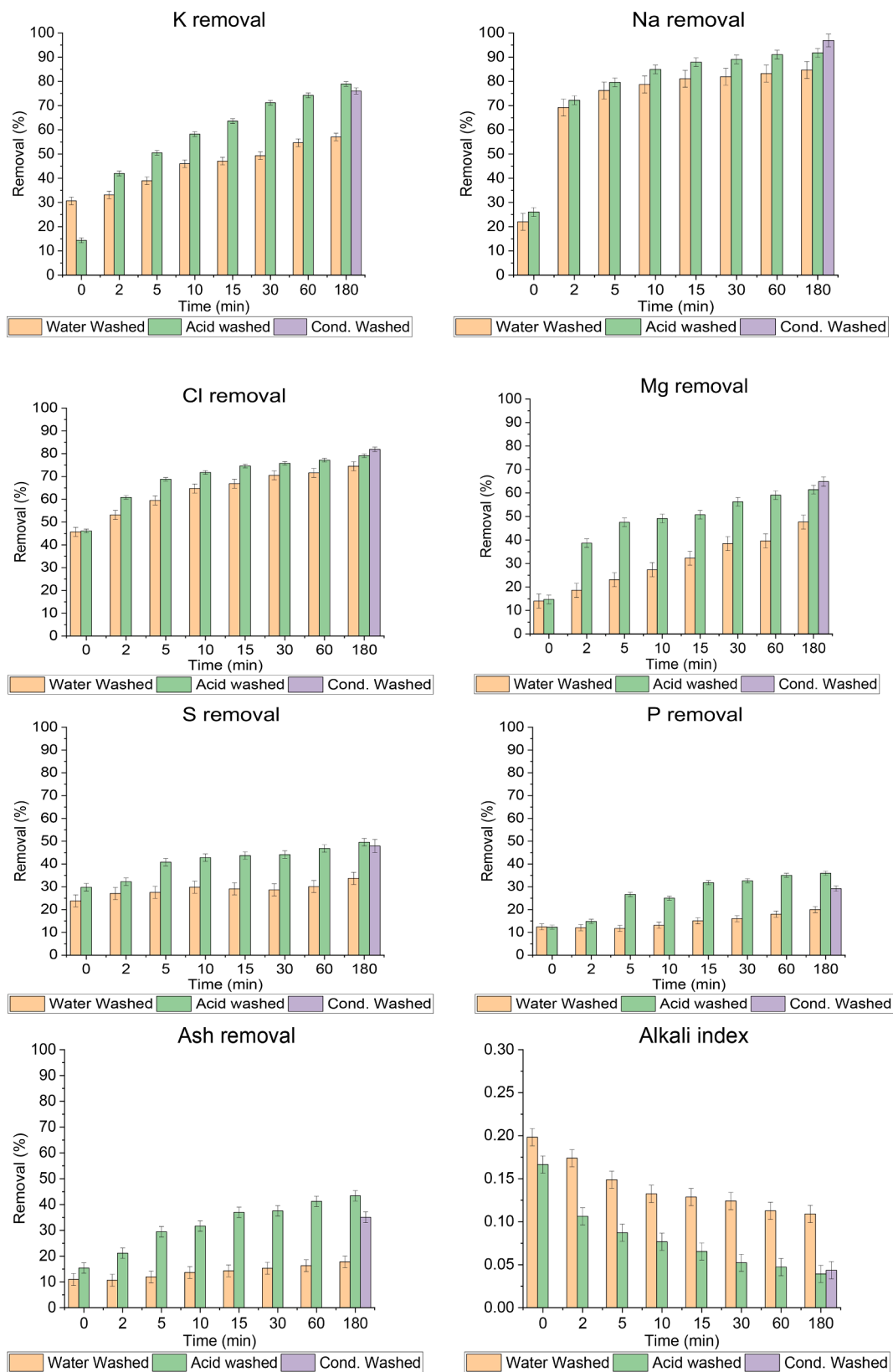


Fig. 2. Effect of leaching duration on removal efficiencies of various troubling elements.

almost unchanged due to high ash removal (Table 2). As a result, energy yields after SEC and acid-washing were slightly higher than water-washing (1–3%).

### 3.2. Effect of washing on removal of troubling elements and alkali index

In Fig. 2, effect of washing medium and washing duration can be seen clearly on different TEs. Continuous removal of all the TEs was

Table 3

Proximate, ultimate, heating value, mass loss, and energy loss analysis of the raw and pre-treated bark (nd = not detected).

| Washing type  | Washing time | MC (%) | VM (%) | FC (%) | Ash (%) | C (%)  | H (%) | N (%) | S (%) | O (%) | HHV (MJ/kg) | Mass yield (%) | Energy yield (%) | Electrical conductivity ( $\mu\text{S}/\text{cm}$ ) |
|---------------|--------------|--------|--------|--------|---------|--------|-------|-------|-------|-------|-------------|----------------|------------------|---|
| Original bark | –            | 1.724  | 75.146 | 19.67  | 3.464   | 48.625 | 5.660 | 0.25  | 0.08  | 42.00 | 19.224      | –              | –                | –   |
| Water         | 0 min        | 1.913  | 75.232 | 19.66  | 3.199   | 48.374 | 5.630 | 0.244 | nd    | 42.55 | 19.050      | 96.43          | 95.56            | 240   |
| Washed        | 2 min        | 1.984  | 75.426 | 19.39  | 3.197   | 48.170 | 5.636 | 0.238 | nd    | 42.76 | 18.965      | 96.81          | 95.51            | 277   |
|               | 5 min        | 1.926  | 75.625 | 19.27  | 3.181   | 48.073 | 5.615 | 0.231 | nd    | 42.90 | 18.892      | 95.89          | 94.24            | 345   |
|               | 10 min       | 2.162  | 75.651 | 19.05  | 3.141   | 48.075 | 5.655 | 0.230 | nd    | 42.90 | 18.941      | 95.25          | 93.85            | 415   |
|               | 15 min       | 2.720  | 75.641 | 18.52  | 3.118   | 48.070 | 5.649 | 0.230 | nd    | 42.93 | 18.929      | 95.22          | 93.76            | 418   |
|               | 30 min       | 2.256  | 75.692 | 18.95  | 3.103   | 48.075 | 5.640 | 0.232 | nd    | 42.95 | 18.918      | 94.56          | 93.05            | 423   |
|               | 1 hr         | 3.040  | 75.782 | 18.08  | 3.098   | 48.076 | 5.610 | 0.235 | nd    | 42.98 | 18.881      | 93.62          | 91.95            | 455   |
|               | 3 hr         | 2.966  | 75.850 | 18.09  | 3.091   | 47.734 | 5.617 | 0.238 | nd    | 43.32 | 18.734      | 92.15          | 89.81            | 526   |
| Original bark |              | 1.911  | 73.97  | 21.19  | 2.93    | 49.100 | 5.736 | 0.332 | nd    | 41.90 | 19.500      | –              | –                | –   |
| Acetic acid   | 0 min        | 1.544  | 75.135 | 20.39  | 2.504   | 49.684 | 5.817 | 0.335 | nd    | 41.66 | 19.834      | 99.03          | 100.72           | 480   |
| washed        | 2 min        | 1.626  | 75.646 | 19.80  | 2.392   | 49.341 | 5.689 | 0.291 | nd    | 42.29 | 19.501      | 96.60          | 96.61            | 588   |
|               | 5 min        | 0.685  | 75.878 | 20.51  | 2.108   | 49.410 | 5.760 | 0.278 | nd    | 42.44 | 19.599      | 96.55          | 98.54            | 606   |
|               | 10 min       | 1.849  | 76.212 | 19.01  | 2.075   | 48.585 | 5.448 | 0.246 | nd    | 43.65 | 18.820      | 96.55          | 93.18            | 672   |
|               | 15 min       | 1.991  | 76.666 | 18.41  | 1.923   | 48.676 | 5.700 | 0.235 | nd    | 43.47 | 19.170      | 96.04          | 94.42            | 717   |
|               | 30 min       | 1.948  | 76.834 | 18.29  | 1.905   | 48.786 | 5.728 | 0.244 | nd    | 43.34 | 19.256      | 96.02          | 94.82            | 745   |
|               | 1 hr         | 0.768  | 77.004 | 19.30  | 1.819   | 48.580 | 5.723 | 0.257 | nd    | 43.62 | 19.150      | 94.69          | 92.98            | 812   |
|               | 3 hr         | 2.067  | 77.224 | 17.78  | 1.798   | 49.413 | 5.756 | 0.244 | nd    | 42.79 | 19.566      | 92.27          | 92.59            | 862   |
| SE Cond.      | 3 hr         | 1.76   | 77.62  | 18.59  | 1.99    | 49.202 | 5.740 | 0.224 | nd    | 42.84 | 19.464      | 95.62          | 95.45            | 1140  |
| washed        |              |        |        |        |         |        |       |       |       |       |             |                |                  |   |

noted on increasing washing duration. After washing, the highest removal was noted for Na, K, and Cl, which ranged from 14 to 46% at 0 min to 57–97% at 180 min. For water-washing, very high and rapid removal was noted till 10 min for most of the TEs. Though beyond 10 min, it further increased by <10%, except for Mg. While for acid washing, similar trends were also seen till 15 min, after which <10% increment was noted, except for K. Similar trend of removal of these elements was also seen in other feedstocks such as pine bark, wheat straw, EFB, and rice straw [17,23,43,47]. As most K, Na, and Cl are present in biomass as water-soluble salts like KCl, NaCl,  $\text{K}_2\text{SO}_4$ , and  $\text{Na}_2\text{SO}_4$ , their removal was much higher than the other elements [3]. Even at 0 min, about 31% K, 46% Cl, and 22% Na removal were seen. At short washing durations (10–15 min), about 46–79% removal of K, Na, and Cl was noted, which increased to 57%, 75%, and 85% after washing for 180 min, respectively. After acid and SEC washing slight improvement (<12%) was seen for Na and Cl removal. However, after acid-washing, about 9–24% more removal of K was observed compared to water-washing. This result was expected since ~ 25% alkali and ~ 10% Cl in spruce bark are only leachable in buffer and acidic medium [3]. As Cl and alkali elements are the root cause of fouling, corrosion, and agglomeration, because of their high removal, much less such issues can be expected from the treated biomass, especially acid-washed bark.

As only a small part of N and S in bark exists as mobile form ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ ) [9,51], up to 12% and 34% removal of both elements, respectively, was noted after water-washing. However, about 20% of S and N in bark only be leachable in acid medium. Therefore, about 5–30% extra removal of N and S was seen upon washing with 0.1 M acetic acid (Figures 2 and S3). Similar to alkali elements, S and N showed continuous removal on increasing leaching duration for water and acid-washing, and minimal increment (<5%) in their removal was noted after 5–10 min of washing. Due to considerable removal of S and N, lesser  $\text{NO}_x$  and  $\text{SO}_x$  emission can be expected from the combustion of the treated material.

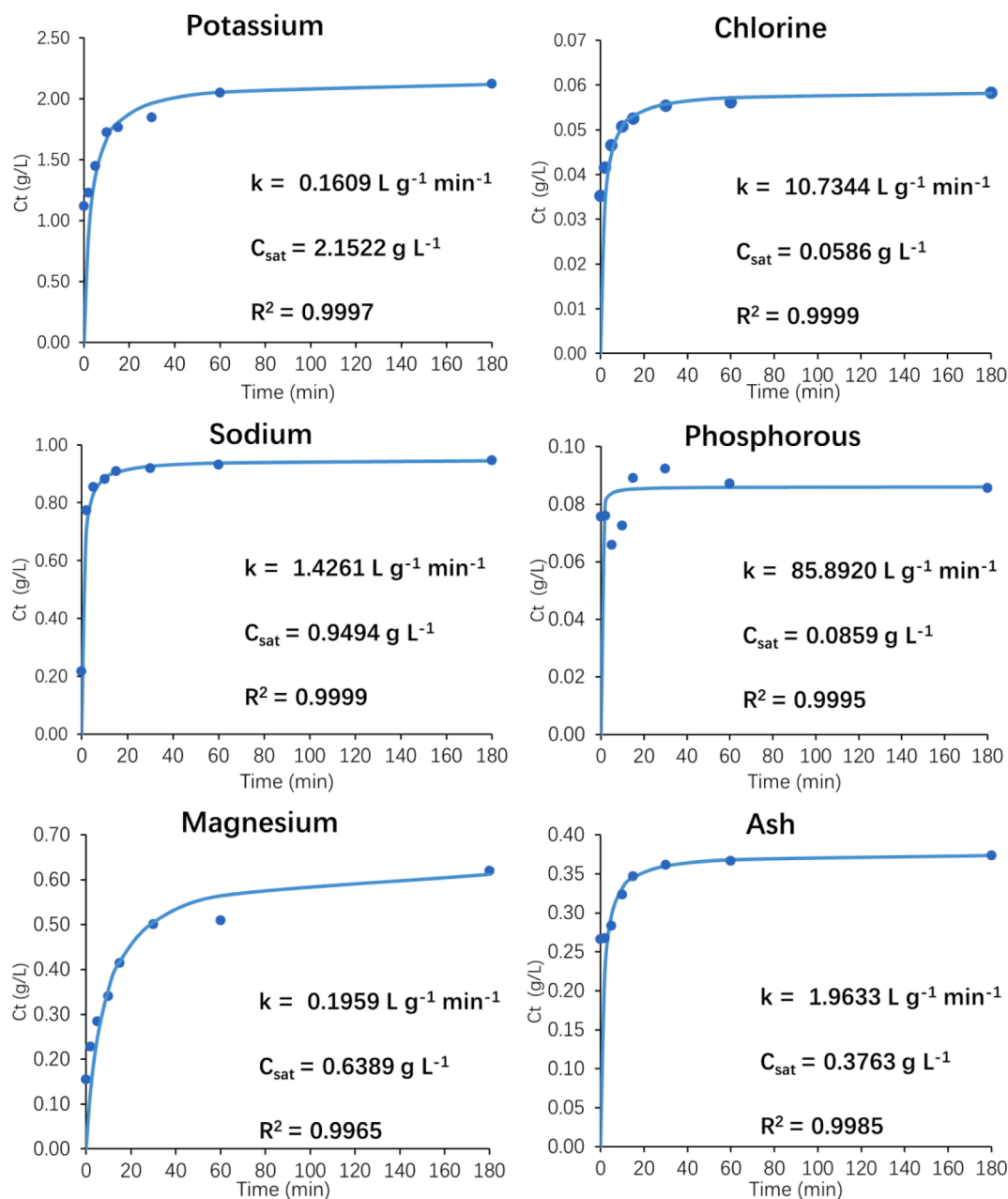
The removal trend of Mg, Si, and P was similar to each other but different from the other elements. Up to 65% Mg, 43% Si, and 36% P removal was achieved after acid washing, while up to 48% Mg, 10% Si, and 20% removal was seen in water washing. An interesting trend in water and acid-washing was the slow and steady increase in removal of these elements at longer washing durations (>15 min). During water-washing, a similar trend for P removal was also reported for wheat straw, mallee wood, and rice husk [51–53]. In water-washing, this extra removal could result from the leached organics such as acetic acid,

propanoic acid, formic acid, lactic acid, sugars, and phenols. These organics facilitate the removal of some ion-exchangeable and acid-soluble inorganic elements which are insoluble in water. Removal of Ca, Mg, K and P due to the leached organics was also noted in past studies for other feedstocks [47,51,53]. Another possible reason behind the steady removal of these elements is the lower solubility of the silicates and salts of Mg (Mg-phosphate, -oxalate, -phytates, -carbonates), and P (phosphates and phytates of Ca and Mg) [9,57]. About 65% Mg, 20% Si, and 35% P present in spruce bark require a buffer or acid solution to be leached from biomass [3], which explains the extra removal of these elements on acid-washing. After water-washing, <10% removal for Ca was achieved, which increased to 22–23% after acid and SEC washing. About 55% removal for Fe was also noted after water-washing, almost independent of washing duration. Fe is not present in high amounts in bark, and most of it is firmly incorporated in biomass and only leaches under severe acidic conditions [3,5]. Therefore, this Fe removal could be a result of the removal of extraneous impurities which adhered to biomass during storage and transportation. Compared to acetic acid, washing with SEC showed only a 5% lower removal efficiency for most elements except Si. Hence, 0.1 M acetic acid was a suitable substitute for SEC for research purposes.

As a result of high leaching of TEs, a significant improvement in the AI was observed, especially after acid-washing (Fig. 2 and Table S2). Just washing for 5 min with water and 2 min with acetic acid, treated bark showed a likelihood of negligible to very less fouling propensity (AI < 0.17). Therefore, much less fouling, slagging, and agglomeration issues can be expected from the treated bark. One crucial point that should be considered while studying AI values is that cut-off values were originally developed for coal [14]. AI values may not be directly applicable for forest and agricultural feedstocks because of differences in composition and mineralogy [10,14,15]. So, instead of the cut-off values, more focus should be given to the trends in AI with removal trends of K, Na, Ca, Mg, P, Cl, and S. Therefore, with reduced AI value and high removal of Cl (<82%), S (<50%), Na (<97%), K (<79%), Mg (<65%) and P (<36%), much less fouling, slagging and corrosion could be expected from the treated bark.

### 3.3. Leaching kinetics of troubling elements

From the results (Figs. 3 and 4), it is visible that most of the TEs and overall ash follows second-order leaching kinetics during water- and acid-washing. The leaching rate for all TEs was very high for short



**Fig. 3.** Leaching kinetics of critical ash elements and ash in water-washing experiments (trend line shown in each graph is of the second-order kinetics model, and the data points are from the experimental results).

durations (<15 min), especially for Cl, P, and S. Though after 30 min of washing, minimal increment in the leached concentration was noted for most TEs except Mg. As no previous study was available on bark for comparison, trends of the present study were compared with leaching kinetics of other biomass samples. Similar K, Na, Cl, and Mg leaching trends were also seen in the water-washing studies of mallee wood [53] and EFB [45]. For water-washing, this second-order leaching behavior of TEs confirms that leaching is a two-stage process. In the first stage, maximum leaching takes place within a short duration as a result of intense dissolution and scrubbing of highly soluble inorganic salts [49]. While in the second stage, the rate of leaching and amount leached were very small. There may be two possible approaches to explain this behavior. First, the slow diffusion of the TEs into the leaching solution is hampered greatly by the increasing concentration of the inorganic species in the leachate [45,49]. Second, the slower leaching facilitated by water-soluble organics, which also leach during washing. As

mentioned previously, the leached organic compounds facilitate the removal of weakly bound and acid-soluble inorganic species. This leaching process is prolonged but persistent, as seen in the previous section (Fig. 2), especially for Mg and P. There is a high possibility that both phenomena are happening in the later part of the leaching process. During acid-washing, slow and consistent removal at longer durations could result from breaking the internal structure and further penetration of acid in the biomass organic matrix. This results in extra removal of organically bound elements such as K, Na, Mg, P, and Ca. Previous studies also noted the breaking of the internal structure due to acid-washing [22,34,35]. Notably, the value of saturated concentration of K, Na, and Mg were higher, showing that they were leached in high amounts. At the same time, the overall leaching rate was highest for Cl and P for both water and acid washing.

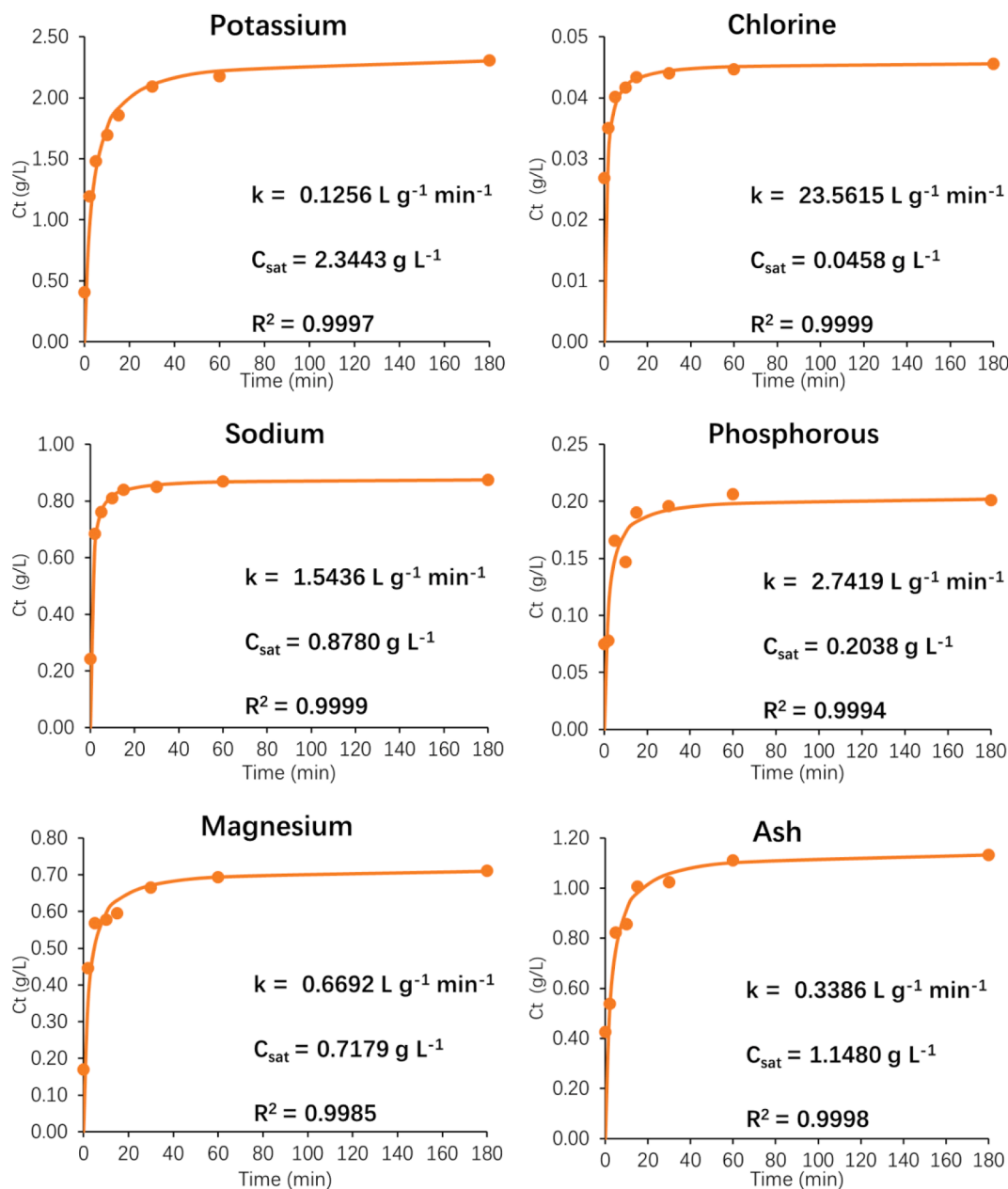


Fig. 4. Leaching kinetics of critical ash elements and ash in acetic acid-washing experiments (trend line shown in each graph is of the second-order kinetics model, and the data points are from the experimental results).

### 3.4. Thermodynamic equilibrium modeling (TEM)

TEM results reveal that after washing pre-treatment, the chemical behavior of spruce bark at higher temperatures changes substantially. As biomass combustion and gasification operating temperatures range between 800 and 1000 °C, compounds formed at these temperatures were studied in detail. Complete TEM results from 500 °C to 1500 °C for raw bark, water-, acid-, and SEC-washed bark samples are included in the [supplementary material](#). While compounds formed at 600 °C, 800 °C, 1000 °C, and 1200 °C are shown in [Fig. 5](#).

After pre-treatment, major changes were noted for AAEM compounds, both at high ( $\geq 1000$  °C) and relatively lower temperatures (500–1000 °C). Major K compounds formed at low temperatures were  $K_2Ca_2(CO_3)_3$  (s),  $K_2CO_3$  (s),  $K_2SO_4$  (s), and  $K_3PO_4$  (s) with some KCl (s) and KCl (g) ([Fig. 5a](#)). The formation of compounds like  $K_2Ca_2(CO_3)_3$ ,  $K_2CO_3$ , KCl, and  $K_2SO_4$  was also seen in other woody biomasses [[38,40](#)].  $K_2Ca_2(CO_3)_3$  was the major compound at 500 °C, which completely

breaks down before 800 °C forming  $K_2CO_3$  and  $K_3PO_4$  in both treated and untreated bark. The concentration of both the compounds peaks at 800 °C, after that they form  $K_2O$  (slag),  $P_2O_5$  (slag), and KOH (g). Between 850 °C and 1200 °C, considerable amount of K exists as molten slag, while most  $K_2CO_3$  and  $K_2SO_4$  exist as molten salt. So, more ash fusion and melting can be expected in raw bark above 850 °C. In the past studies [[14,16,58](#)],  $K_2CO_3$ ,  $K_2SO_4$ , and KCl were found major reason behind ash-melting and ash-deposition-related issues. Furthermore, after 900 °C majority of the K releases as KOH (g) with some KCl (g) and  $K_2SO_4$  (g). Both KCl and  $K_2SO_4$  are already well-known for their major role in fouling and corrosion of heat exchangers [[14,58](#)]. Yet the role of KOH in fouling and corrosion is still unclear and requires further research. However, some studies show that KOH acts as a reaction intermediate in forming KCl,  $KHSO_4$ , and  $K_2SO_4$  in the presence of HCl,  $SO_2$ , and  $SO_3$ , eventually leading towards fouling and corrosion [[58–60](#)]. Therefore, due to the formation of molten slag and gaseous K compounds, some fouling-, corrosion-, and slagging-related issues can



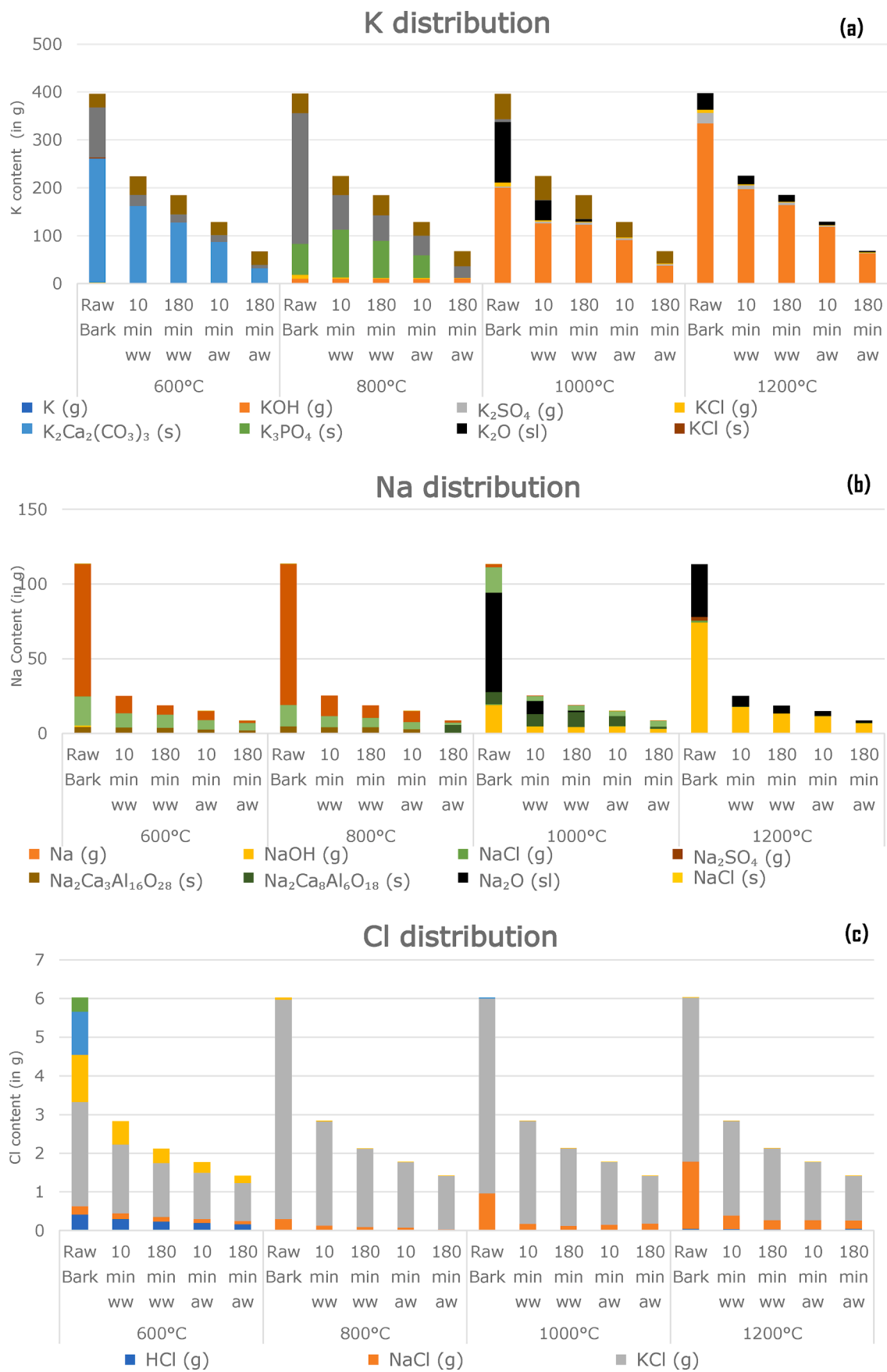


Fig. 5. (a-f) Distribution of troubling elements in various compounds (sl – slag, s – solid and g – gas) (g) total amount of slag formed at different temperatures as per thermodynamic equilibrium modelling results.

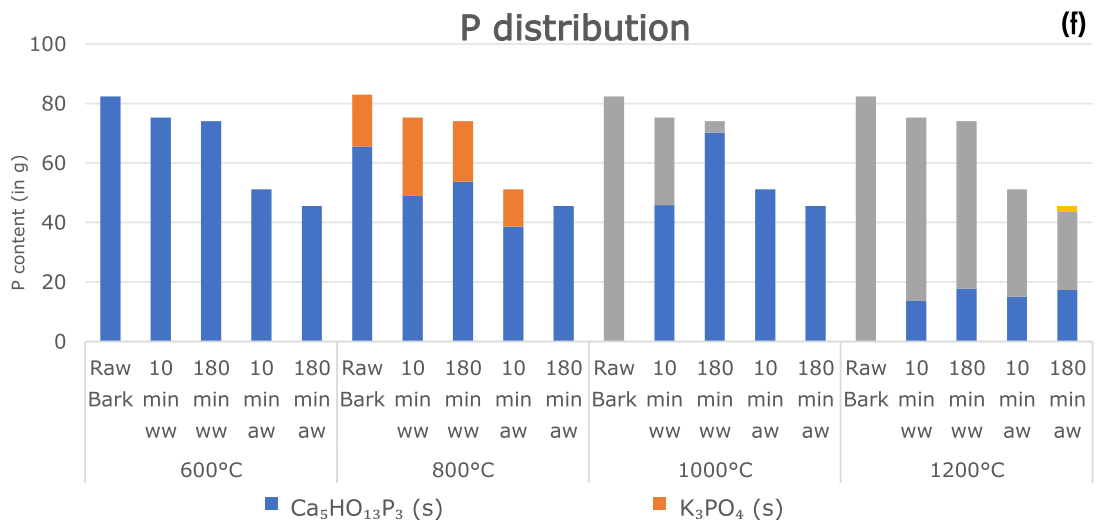
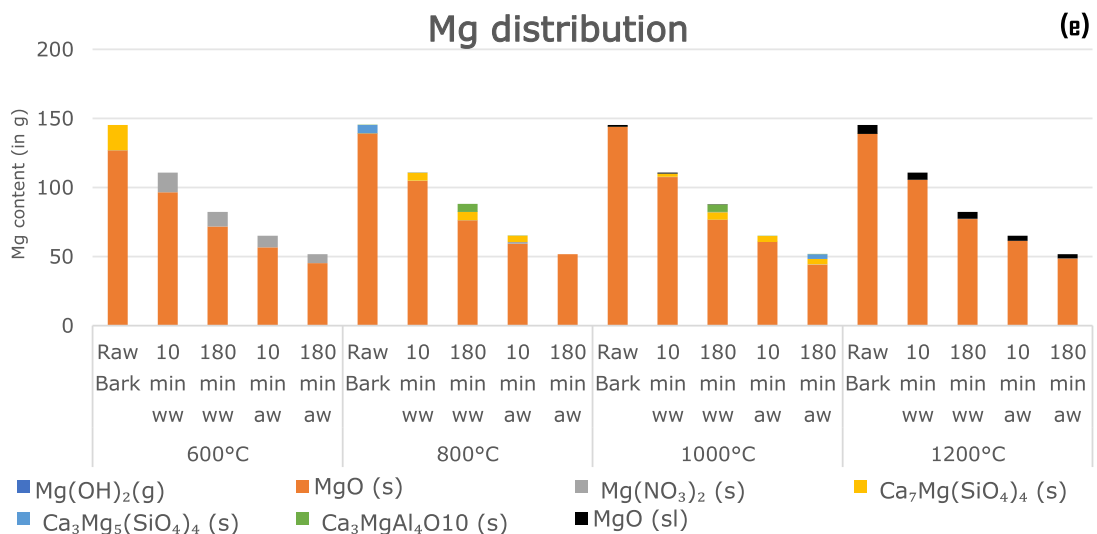
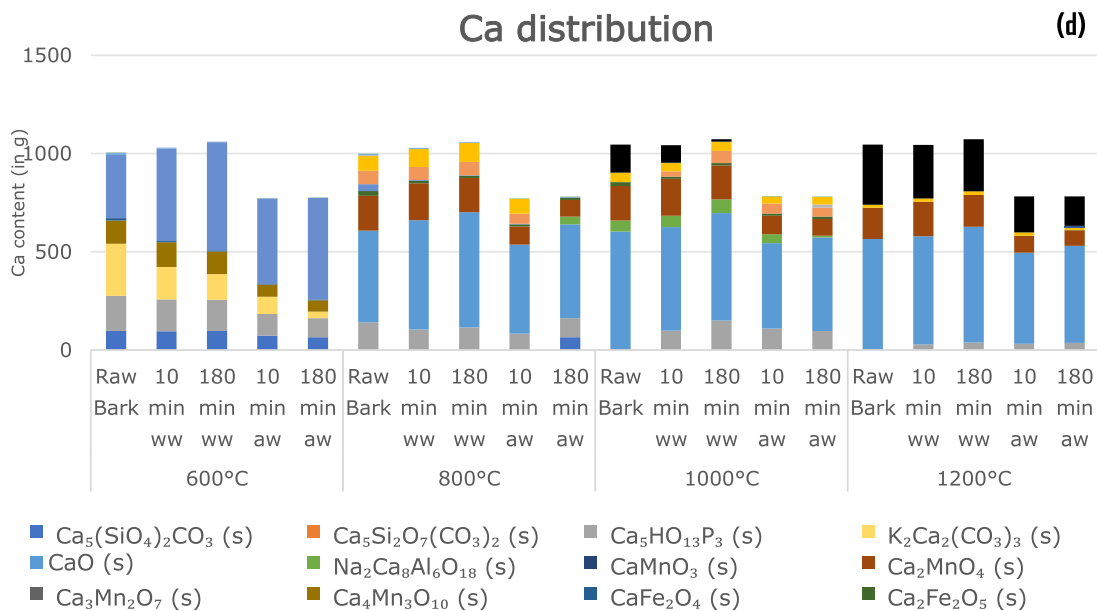


Fig. 5. (continued).

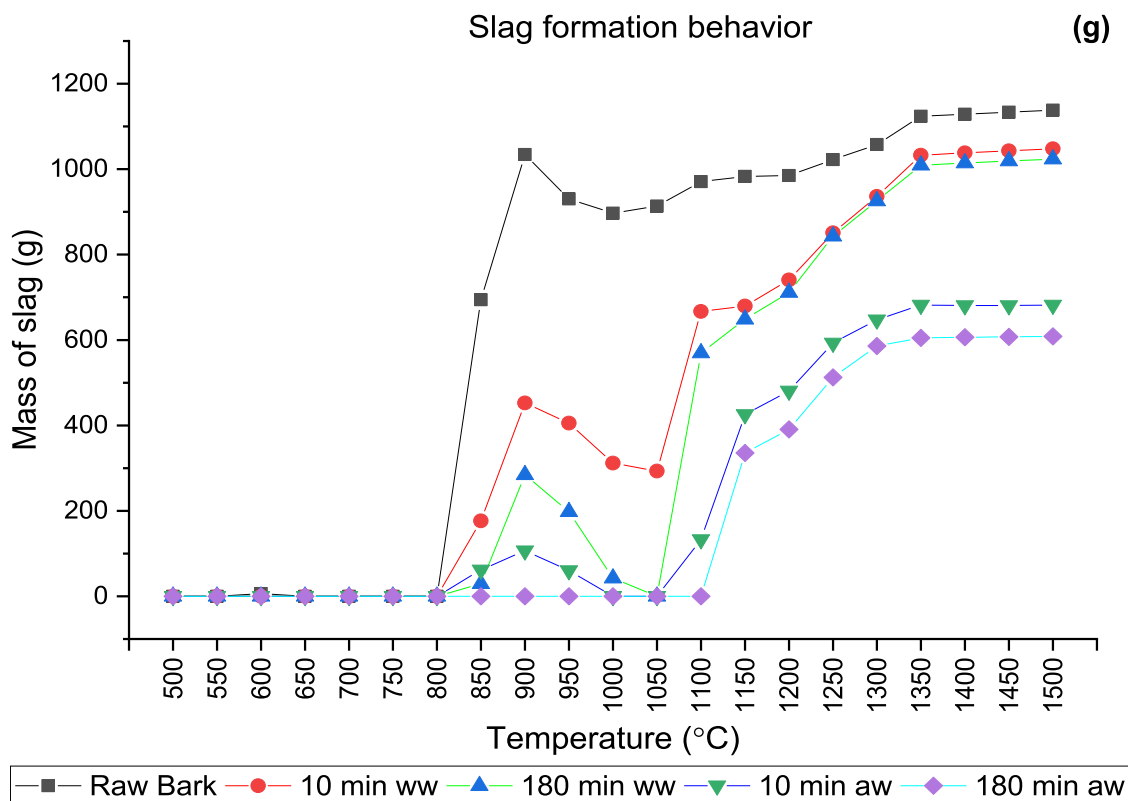


Fig. 5. (continued).

be expected from the bark. However, it is important to mention that overall amount of K in the spruce bark is very less (<0.5%), so even with the abovementioned species only minimal to medium fouling can be expected from the spruce bark.

After washing pre-treatment, a substantial change in the chemical species can be seen at higher temperatures. As washing results in high removal of K, much less problematic K species were formed, especially in the case of acid-washing. At lower temperatures (500–1000 °C), major compounds seen in raw bark were also formed in washed bark. However, their amounts were substantially less and continuously declining with the increasing pre-treatment intensity (Fig. 5a). The major change noted at the lower temperatures was the content of  $K_2CO_3$ , which continuously decreased with increasing washing intensity. Furthermore, at 800 °C, minimal  $K_3PO_4$  was formed in 10 min acid-washed sample while it completely vanished from the 180 min acid-washed sample. It resulted from high P removal in the acid-washed samples (Figs. 2 and 5). At higher temperatures (>1000 °C), one of the major benefits of washing seen was the formation of negligible to the small amount of  $K_2O$  (slag) and continuous reduction in KOH (g) content. Specifically for acid-washed and 180 min water-washed samples, the amount of slag, KCl (g), and  $K_2SO_4$  (g) were negligible to very less (Fig. 5a). As a result, much less fouling, corrosion, slagging, and ash melting can be expected from the washed bark, especially acid-washed bark.

As Cl tends to react first with K, most of Cl in treated and untreated bark is released mainly as KCl (g), with some as NaCl (g) and HCl (g) (Fig. 5c). Cl compounds are the major reason behind corrosion and fouling issues in the boiler. However, as the amount of Cl in the bark is low, much less participation can be expected from the Cl compounds. Furthermore, as >80% Cl were removed after washing, fewer ash-related issues can be expected after treatment.

The behavior of Na compounds was almost similar to K compounds formed between 500 °C and 1500 °C. Major compounds formed in raw bark at lower temperatures (500–1000 °C) were  $Na_2CO_3$  (s),  $Na_2SO_4$  (s),  $Na_2Ca_3Al_6O_{28}$  (s) with a trace amount of NaCl (s). Before 850 °C,

$Na_2CO_3$  was the major compound that breaks into  $Na_2O$  (slag) and  $CO_2$  (g) after 850 °C.  $Na_2O$  slag peaks between 900 and 1000 °C which transform into NaOH (g) at higher temperatures. Both K and Na show the highest amount of slag in raw between 900 °C and 1000 °C. Similar to K-compounds, Na compounds like  $Na_2CO_3$ ,  $Na_2O$  (slag), and  $Na_2SO_4$  are expected to cause slagging and ash-melting related issues in high-temperature applications, which are also noted in other studies [14]. After washing, >80% Na was removed. Consequently, the amount of Na compounds formed is much less than raw bark. Like K, Na compounds formed in washed biomass following the same trends as raw bark except for acid-washed samples. Acid-washed sample form minimal  $Na_2O$  slag and NaOH (g) at high temperatures.

An apparent effect of washing can be seen on P-compounds formed at higher temperatures. Almost all the P in biomass is retained in ash, which was also noted in previous studies [38]. At low temperatures, the primary product in both treated and untreated bark was hydroxyapatite ( $Ca_{10}(PO_4)_6(OH)_2$  (s) or  $Ca_5HO_{13}P_3$ ). After 850 °C, all the P in raw bark exists as  $P_2O_5$  (slag), which changes completely for washed bark, where the major product was still hydroxyapatite until 1100 °C. Also, a considerable amount of P was leached in acid washing, due to which not much formation of P compounds and slag were noted at the higher temperatures.

Mg mainly exists as MgO (s) in both washed and raw bark samples at all temperatures. Between 600 and 800 °C,  $Ca_7Mg(SiO_4)_4$  and  $Ca_3Mg_5(SiO_4)_4$  are other main compounds besides MgO. In washed bark samples,  $Mg(NO_3)_2$  forms between 500 °C and 750 °C, which breaks completely at 800 °C. Raw and water-washed bark started to form very trace amounts of MgO (slag) at 1000 °C which further increased the high temperatures. Whereas acid-washed samples show notable formation of MgO (slag) only after 1150 °C. Though, all the samples showed considerable amounts of MgO (slag) after 1200 °C. After washing slight reduction in MgO (slag) was also seen at higher temperatures than raw bark.

Between 600 °C and 800 °C major Ca compounds formed were the

same for raw and treated bark samples though their content differed considerably. Until 750 °C, calcite (CaCO<sub>3</sub>) was the main compound in all samples, which breaks suddenly at 800 °C into CaO (s) and CO<sub>2</sub> (g). Similar behavior was also seen in TEM of other woody biomasses [38,40]. Other major compounds formed between 600 and 800 °C were CaO, CaNO<sub>3</sub>, K<sub>2</sub>Ca<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>, Ca<sub>5</sub>HO<sub>13</sub>P<sub>3</sub>, Ca<sub>4</sub>Mn<sub>3</sub>O<sub>10</sub>, and Ca<sub>2</sub>MnO<sub>4</sub>. Due to the removal of 14–18% Ca in acid-washed samples, amounts of these compounds formed were also less for the acid-washed samples. After 850 °C, some CaO (slag) started to form in raw bark, continuously increasing with rising temperature making 30–40% of total Ca-derived compounds at 1300–1500 °C. 10 min water-washed samples followed similar trends with a lesser amount of Ca-slag. While 180 min water and acid-washed samples show major slag formation only after 1100 °C in much lesser amounts than raw bark. Most Ca, Mg, and Si compounds have high melting points (>1100 °C) and do not participate in ash-related issues. However, some Ca, Mg, Si, and Al compounds react with K and Na to form low melting eutectics (600–800 °C) [14]. As acid-washing results in high K removal and considerable Ca removal, much less fouling and slagging can be expected from the treated bark.

All the above-mentioned results clearly indicate that washing remarkably reduces the content of problematic species and molten slag, reducing fouling, slagging, and corrosion propensity of the bark. Most raw bark elements (K, Na, Ca, and P) already show slag formation at 850 °C. K, P, and Na, slag amount peaks between 800 and 900 °C, while for Ca and Mg, it peaks at higher temperatures (>1300 °C). Washing reduces the amount of slag formed for all the elements and delays the slag formation temperatures. As a result, net slag amount is reduced greatly after washing specially for acid washed bark. Increment in the ash fusion temperatures after washing pre-treatment was observed in previous studies, resulting from delayed and reduced formation of molten slag [14]. Between 1000 and 1050 °C net slag amount is decreasing for all the samples which is the result of gradual breaking of compounds such as K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, CaNO<sub>3</sub> and Na<sub>2</sub>Ca<sub>8</sub>Al<sub>6</sub>O<sub>18</sub>. Therefore, these temperatures can be preferred for combustion and gasification of treated bark for fewer ash-melting and slag formation related issues. The best results were seen for 180 min water-washed and acid-washed samples, which can be seen in Fig. 5 and S4–S9. As the leaching efficiency of SE condensate is similar to acetic acid washing, both show very similar trends in the TEM (Figure S4–S9).

### 3.5. Critical comments, recommendations for industrial applications, and further scope

All the results clearly indicated that both water and acid-washing considerably reduced the inorganic content of spruce bark. Compared to water, acid-washing shows a much higher removal of the TEs. Both AI and TEM shows substantial reduction in the formation of problematic AAEM compounds and slag at high temperatures. As a result, fewer issues related to fouling, corrosion, slagging, and ash melting can be expected from the treated bark in combustion and gasification. As bark contains very small amounts of Fe and S compounds, similar behavior in the transformation of ash compounds can be expected in the reducing atmosphere [40]. So, the result from the present study can also be used for assessing various ash-related issues in gasification. However, it is essential to mention that TEM mainly provides the trends in the transformation behavior of the ash elements, which can be used to predict ash-related issues. Factsage allows to estimate the ash chemistry and gives an insight into the molten fraction based on the feedstock composition and Gibbs free energy minimization principle. However, for quantitative analysis the accuracy of TEM can be improved by comparing it with experimental data and modifying the model using appropriate factors, coefficients, and careful selection of databases [43]. To the best of our knowledge, none of the related research work explored calibrated/constrained TEM, thus creating future research opportunities. Though based on previous literature [38–40,42,43,61], TEM can be successfully used for initial assessment regarding ash

transformation behavior and subsequently predicting various biomass ash-related issues in high-temperature applications.

Best results of washing were seen either at long washing durations with water or washing with acid. Though for large-scale industrial applications, both longer washing duration [25,51] and high quantities of acid may not be economically and environmentally sustainable. For such cases, SEC can be used for better washing efficiency for short washing durations as it primarily comprises acetic acid. Integrating SEC and SE pretreatment could be sustainable approach. However geographically, the availability and transportation of SEC may be challenging. So, the sustainability of utilizing SEC and acetic acid needs to be evaluated case-by-case. In general for practical applications and high washing efficiency, washing for 10 min with SEC or 0.1 M acetic acid should be sufficient.

Although washing is a simple and effective method to improve fuel quality, some issues require further attention for successfully implementing it on a larger scale. Two major challenges related to washing pretreatment are drying requirements for wet biomass and handling the wastewater or leachate, especially from acid-washing since it may be corrosive. The treated feedstock contains 40–70% water, which needs to be removed before thermochemical conversion. Even though mechanical pressing and hot-stock gases [51] can reduce the moisture content, further research is still required. Regarding wastewater treatment, a detailed characterization of the wastewater is needed, which is challenging due to the heterogeneity of biomass composition and AAEM distribution. Recovery of the acids, furfural, and elements (N, P, Mg, K) may be another possible approach for handling wastewaters. Few studies report wastewater from pre-treatment contains high amounts of COD, TOC, salts, and nutrients [25,62] and it could be treated through RO [62]. However, using RO for the large-scale plant may not be economical due to high capital costs and high reject water. So, the wastewater treatment requires further attention, which is ongoing in our lab and will be presented as a separate article.

## 4. Conclusion

In the present study, the effect of water, acetic acid, and steam explosion condensate (SEC) washing on the inorganic composition of spruce bark was studied comprehensively. Furthermore, to understand the leaching behavior and high-temperature transformation behavior of troubling elements (TE), leaching kinetics and thermodynamic equilibrium modeling (TEM) were also performed. The following major conclusions can be drawn from the present study:

- Both water and acetic acid washing show very high removal of all the TEs from spruce bark. Up to 85% Na, 75% Cl, 57% K, 48% Mg, 34% S, 20% P, 18% ash, 12% N, 10% Ca, and 10% Si removal was noted from water washing. While up to 92% Na, 79% Cl, 79% K, 61% Mg, 50% S, 43% ash 43% Si, 36% P, 32% N and 22% Ca removal was achieved after washing with 0.1 M acetic acid solution. Continued removal of TEs was noted with increasing washing duration in water and acid washing.
- Acetic acid washing shows relatively higher and quicker removal of the TEs. SEC shows similar leaching efficiency for most TEs as 0.1 M acetic acid. Hence, acetic acid can simulate SEC washing for research purposes.
- Most TEs (K, Na, Cl, S, P, and ash) show second-order leaching kinetics, which shows that washing is a two-step process. In the first step, rapid removal of TEs was noted, which occurred at short washing durations (<15 min). After 15–30 min, the leaching rate was almost negligible to very slow.
- The result of TEM shows that ash transformation behavior improves substantially after pre-treatment, most remarkably for acid-washed samples. Raw bark shows notable amounts of chemical compounds and molten slag responsible for alkali-induced fouling and slagging, especially at higher temperatures (850–1100 °C) such as KCl, K<sub>2</sub>SO<sub>4</sub>,

$K_2CO_3$ , KOH,  $Na_2SO_4$ , NaCl, etc. Both water and acid washing considerably reduces the formation of such problematic compounds and molten slag. So, based on TEM, much less fouling and ash-related issues can be expected from the washed bark at typical combustion and gasification temperatures (800–1100 °C), especially from acid-washed bark.

- Though best water and acid washing results were seen for longer washing duration, for practical applications, 10 min washing with acetic acid or SE condensate is recommended.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

No data was used for the research described in the article.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2022.139351>.

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