Case Studies in Chemical and Environmental Engineering 9 (2024) 100568

Contents lists available at ScienceDirect

Case Studies in Chemical and Environmental Engineering

journal homepage: www.sciencedirect.com/journal/case-studies-in-chemical-and-environmental-engineering

Thermodynamic analysis on the thermal treatment of spent alkaline batteries-PVC blends under inert conditions

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ARTICLE INFO

Keywords:
Battery waste recycling
PVC recycling
Thermodynamics
Solubility
$ZnCl_2$
$MnCl_2$

ABSTRACT

Polyvinyl chloride (PVC) and Spent Alkaline Batteries (SAB) are produced and accumulated in large quantities. The absence of a sustainable recycling route for these wastes amidst a circular economy era makes it important to find a potential coupling route of their waste streams into useful products. Herein, the behaviour of zinc, manganese, and iron were tracked through a thermodynamics calculation of the thermal treatment of PVC mixed with SAB followed with a thermodynamic assessment of the leaching of the pyrolysis residues. thermodynamics calculations suggest that zinc and manganese can be extracted with a percentage of up to 100% if PVC is thermally treated with water washed SAB under pyrolytic conditions at a temperature of 300 °C. The residues from the thermal treatment (rich in zinc and manganese chlorides) should be then water leached (pH = 5 – 6) to recover Zn^{2+} and Mn^{2+}. Water washing of the SAB should help in suppressing the extraction of both sodium and potassium as they can be omitted from the reaction system when SAB is washed with water. However, the major drawback under the conditions above is that iron will still be extracted with zinc and manganese which can potentially cause complications in the separation at a further stage. Nonetheless, this work lays the foundation for further studies (theoretical and experimental) related to the extraction of zinc and manganese from SAB by means of thermally treating it with waste PVC.

1. Introduction

Spent batteries (SB) are accumulated at an alarming rate due to their extensive use motivated by the great growth in the use of mobile electronic equipment. Portable alkaline and zinc-carbon based batteries are used mainly for household electronics such as cameras, watches, radios, toys and calculators; they form about 70% of the number of portable batteries (64% on mass basis) [1]. About 225,000 tonnes (equivalent to 11 billion batteries) in the European Economic Area (EEA) were placed on the market in 2016, of which 98,000 tonnes of SB were collected, presenting a rate of collection of 44% [1]. The major components of batteries are MnO_2 (positive electrode), Zn (negative electrode), an electrolyte which may contain KOH, $ZnCl_2$ and NH_4Cl, and the steel casing. The increase in the production of batteries is followed with an increase in SB wastes, which will require large landfill sites [2,3]. The Toxicity Characteristic Leaching Procedure (TCLP) test was utilized on 36 SB in a study performed by Karnchanawong and Limpiteeprakan [2]. It was shown that increasing SB disposal in landfills will result in the leaching of metals such as Zn and Mn into the environment, leading to an increase in heavy metal content in landfills leachate [2]. Hence, several researches have been focusing on finding a sustainable recycling route of SB. Generally, an SB is composed of steel, brass and black mass fractions [4]. The steel and brass portions are recycled in existing industrial processes [4]. However, since the black mass portion is composed, primarily, of zinc and manganese oxides, researches have been focusing on extracting these metals by means of hydro [5–10] and pyrometallurgical [4,6,10–14] processing routes. In the former, oxides are dissolved in either acidic [8,15–17] or basic [9,18–20] medias after which the target metal are extracted by precipitation (electrolysis). The major drawback of the hydrometallurgical approach is the resistive nature of manganese bearing oxides exhibiting an exceptionally refractory nature in alkali solutions (extracted at 0.1% in NaOH solution) [14,18]. In acidic medium, manganese was also not extracted completely; extraction yields of 40, 20, and ~27% were reported by Buzatu et al. [20], Ferella et al. [15], and de Souza et al. [5], respectively. However, manganese recovery can be improved if applying reductive leaching, but at the expense of selectivity [14]. The pyrometallurgical technique, in contrast, relies on separating metallic values

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https://doi.org/10.1016/j.cscee.2023.100568
Received 17 October 2023; Received in revised form 21 November 2023; Accepted 26 November 2023

by selective volatilisation of a certain element over the other post reduction. This technique requires extremely high reaction temperatures in order to drive the reduction reactions forward. For instance, reaction holding temperatures of 900 – 1200, 1000, and 950 °C were used by Ippolito et al. [12], Belardi et al. [21], and Ebin et al. [13], respectively for the separation of zinc from the original black mass. Such data suggests that the pyrometallurgical approach is energy intensive and alternative recycling routes should be considered. Recently Aras and Kıral [22] studied the recovery of Zn and Mn via combustion of black mass SAB at a temperature of 750 °C, followed by two stage leaching; in the first stage, the burnt black mass was leached in sulphuric acid achieving 100% Zn recovery, and only 58% Mn was recovered. To completely recover Mn, a reductive leaching using ferric ions in sulphuric acid was applied. Such a process, although provided complete recovery of both metal values, it required high temperature thermal treatment followed by two stage leaching.

Parallel to SB waste stream plastic waste materials are accumulated worldwide in large quantities. Poly vinyl chloride (PVC) is a heavily produced plastic material and the abundance of this material at the end of useful life makes its disposal a real challenge. About 4.7 million tons was the converters plastic demand of PVC in Europe in the year 2020 [23]. Such large production/recycling rate can be assigned to the highly resistive nature of the material to water and weather conditions [24] and to its superior mechanical properties. Conventionally, PVC is either landfilled or incinerated. Landfilling cannot be considered a sustainable route due to the stability of PVC in landfills (i.e., does not dissociate/degrade) [25] which will occupy vast dumping areas. The major driving force for the incineration approach is the large energy content in the polymeric materials allowing the “waste to energy” approach to be realised [26]. Due to the high chlorine content in PVC, however, this approach should be adapted with caution and with the correct type of additives to mitigate the toxic HCl and chlorinated hydrocarbons emitted in the process. Recently, many research studies have reported that the incineration of PVC wastes in the presence of certain metal oxides have direct impact on the decomposition temperature of PVC [27] and on the nature of emitted gases resulting from the decomposed PVC [28–30]. Furthermore, these metal oxides were reported to have high capacity to capture the emitted HCl during incineration process [31,32]. Therefore, some metal oxides have a catalytic effect on PVC decomposition [33,34].

Herein, a thermodynamics investigation is carried out to assess the feasibility of the co-thermal treatment of PVC with black mass spent alkaline batteries (SAB) under pyrolytic conditions for the extraction of both zinc and manganese. Currently, there is no literature reporting the co-thermal treatment of SAB-PVC wastes making the assessment presented in this work first of its kind. The thermodynamic simulation was carried out using Facility for the Analysis of Chemical Thermodynamics (FactSage) software. Thermal treatment of SAB-PVC mixture is expected to result in capturing HCl emission from PVC by metal oxides present in SAB. This will solve the main environmental problem of HCl emission experienced during conventional PVC waste incineration and simultaneously converts the metal oxides present in SAB to their chloride counterparts making which are water soluble (i.e. more accessible for extraction).

2. Methodology

2.1. Solid state thermodynamics calculations

FactSage software was used to calculate the change in the standard Gibbs free energy (ΔG°) for the expected reactions during the pyrolysis of SAB-PVC mixtures. FactSage was also utilized to identify the expected species and calculate their equilibrium amounts in the temperature window 200-1000 °C. The initial temperature of 200 °C was selected based on the fact that upon the pyrolysis of similar blends to SAB-PVC, the decomposition of PVC begins at about 230 °C, whereby the release of HCl starts [35]. The mineral composition of the SAB used in the current work was estimated based on elemental chemical and X-Ray diffraction (XRD) analyses reported by Hu *et al* [4] as presented in the supplementary material (Fig. S1 and Table S1). The mineral composition of SAB was reported to contain zinc oxide (ZnO), zinc manganese oxide ($ZnMn_2O_4$), hausmannite (Mn_3O_4), graphite (C) and sylvite (KCl), while the major elements reported in SAB were Mn (34.8%), Zn (24.3%), C (8.7%), K (6.2%), Cl (1.6%), Na (2.4%), and Fe (1.0%) [4]. Based on that, the following component composition was estimated (Table 1) and used for the equilibrium thermodynamic calculations for both unwashed and water washed black mass. The purpose of washing the black mass was to remove soluble salts; it was reported that washing would reduce the complications of metals extraction after thermal treatment [9].

The material inventory of alkaline reported by Spanos *et al* [36] (see Table S2 in) was used as a guide to estimate the unexhausted initial components of anode and cathode (KOH and NaOH). In Tables 1 and it was assumed that 90 % of the initial content of MnO_2, in the unused battery, was converted to Mn_3O_4, while the rest was in the form of $ZnMn_2O_4$. It was also assumed that all initial zinc was converted to its oxide form, part of which was in the form of $ZnMn_2O_4$ and the residual was in the form of ZnO. All chloride content was assumed to be in the form of KCl and the rest of potassium was in the form of KOH. Finally, sodium was assumed to be in NaOH form, while iron was assumed to be in the form of Fe_2O_3.

The equilibrium calculations were performed based on a constant mass of SAB black mass (100 grams), while, the content of PVC in the blend was assumed to yield 58% HCl and 10% char based on our previous work [35]. The amount of PVC used was estimated to yield the equilibrium amount of HCl to convert all the present oxides and hydroxides to their chloride forms according to the Reactions 1 – 7.

The SAB-PVC mixtures considered in this work are shown in Table 2; the first mixture contains SAB black mass without washing, while the second mixture did not contain any water soluble matter (washed). The calculation parameters were set at a pressure of 1 atm. Phases formed at values below 0.1 g were ignored from further analysis.

2.2. Water leaching thermodynamics calculations

A thermodynamic speciation analysis was performed on the post pyrolysis residues generated from the thermal treatment of the washed and unwashed SAB-PVC mixture. This is to confirm the possibility to extract both zinc and manganese by water leaching. The amounts of chlorides ($ZnCl_2$, $MnCl_2$, $FeCl_2$, Na_2ZnCl_4, and KZn_2Cl_5) generated from the FactSage simulation were introduced in the water leaching simulation (as a mixture of chlorides). The software used for the leaching simulation analysis was Visual MINTEQ 4.0. In the simulation, the chlorides were introduced as “finite solids” present in an aqueous medium, whereby, the pH of that medium was swept from 0.5 to 14.0 with a step size of 0.5. The leaching was simulated at a temperature of 25 °C (room temperature leaching), with a solid to liquid ratio of 1 g total chlorides dissolved in 100 mL solvent. The feeding material for the simulation is shown in Table 3.

The percentage of Zn^{2+}, Mn^{2+}, and Fe^{2+} dissolved was calculated

Table 1
Component composition of SAB used in the calculations.

Component	Normalized content, grams	
	Unwashed	Washed
Mn_3O_4	42.78	42.78
$ZnMn_2O_4$	7.05	7.05
ZnO	27.36	27.36
C	8.56	8.56
KOH	6.37	0
KCl	2.43	0
NaOH	4.06	0
Fe_2O_3	1.41	1.41

Table 2
SAB-PVC mixtures considered for thermodynamic calculations.

Mixture designation	SAB content, g	PVC content, g	HCl content, g	C content, g
UW-SAB-PVC	100	145.94	85.12	14.59
W- SAB-PVC	87.15	132.52	77.29	13.3

All the calculations were performed under a pyrolytic inert atmosphere (i.e., O_2 concentration was assumed to be zero).

Table 3
Feeding materials for the water leaching simulation, volume of solvent and thermodynamic data associated with the dissolution in water.

Solid phase	Quantity, mmoles	Volume of solvent, mL	$\log(K_{sp})$ at 298.15 K	ΔH_r, kJ/mol at 298.15 K
$ZnCl_2$	2.81	100	7.05	– 72.5
$MnCl_2$	4.76		8.60	– 72.7
$FeCl_2$	0.14		6.80	– 81.5
Na_2ZnCl_4	3.46		8.4	– 60.8
KZn_2Cl_5	9.98		12.9	– 129.6

and used to calculate their recovery. The thermodynamic data such as the solubility product K_{sp}, and the heat of reaction ΔH_r were calculated for $MnCl_2$, $FeCl_2$, Na_2ZnCl_4, KZn_2Cl_5 since they were not present in the original database. Similar calculations were also performed for the potential precipitants such as NaOH, KOH, Na_2O, and K_2O as they were not present in the database. This was done by calculating the change in the standard Gibbs free energy for the dissolution reactions (see section 3.2.6) followed by using the equilibrium rate constant equation:

$$K_{sp} = \exp\left(-\frac{\Delta G^o}{RT}\right) \quad (1)$$

Where ΔG^o is the change in the standard Gibbs free energy (J/mol), R is the universal gas constant (8.314 J/mol.K), and T is the temperature (K). ΔG^o and ΔH^o values were obtained from the database of the FactSage software.

3. Results and discussion

3.1. Change in Gibbs free energy for the main reactions

Reactions 1 – 7 below are the major reactions predicted to occur during the pyrolysis of PVC in presence of SAB. Fig. 1 shows the change in standard Gibbs free energy for these reactions in the temperature range 200 -1000 °C at a step of 10 °C. Reactions 1, 2 and 7 are thermodynamically preferable up to a temperature of 665, 622, and 940 °C, respectively. These reactions involve the chlorination of either manganese (Reactions 1 and 7) or the zinc associated with manganese (Reaction 2). However, the chlorination of zincite (Reaction 3) is thermodynamically possible over the whole studied temperature range. This also applies to Reactions 4 and 5 (chlorination of sodium and potassium hydroxides) and Reaction 5 (potassium hydroxide chlorination) being favourable over Reaction 4. The chlorination of hematite (Reaction 6) is only thermodynamically preferable below a temperature of 132 °C which acts positively towards the selective chlorination of zinc and manganese.

$Mn_3O_4+8\ HCl=3\ MnCl_2+4\ H_2O+Cl_2$ Reaction 1

$ZnMn_2O_4+8\ HCl=2\ MnCl_2+4\ H_2O+Cl_2+ZnCl_2$ Reaction 2

$ZnO+2\ HCl=H_2O+ZnCl_2$ Reaction 3

$NaOH+HCl=H_2O+NaCl$ Reaction 4

$KOH+HCl=H_2O+KCl$ Reaction 5

$Fe_2O_3+6\ HCl=2\ FeCl_3+3\ H_2O$ Reaction 6

$Mn_3O_4+2\ HCl=MnCl_2+Mn_2O_3+H_2O$ Reaction 7

3.2. Thermodynamic calculations on anticipated species

The chemical composition for SAB reported in Table 1 was used to calculate the equilibrium quantities of the predicted chemical species

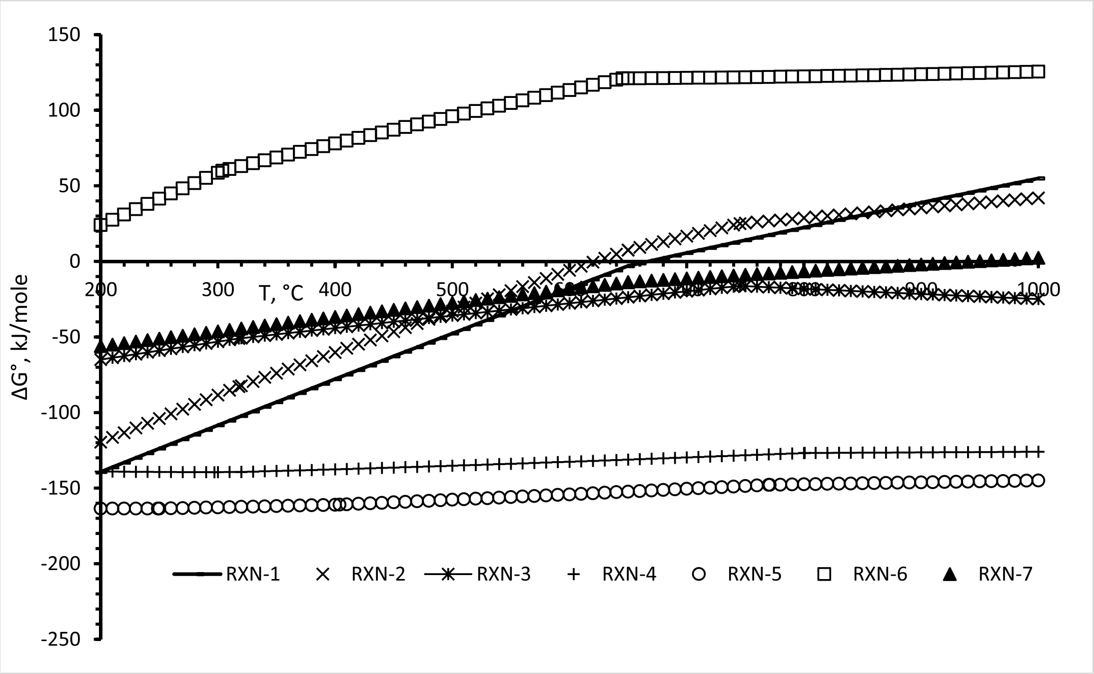

Fig. 1. Standard Gibbs free energy change for the main chlorination reactions calculated using FactSage 7.3 reaction module in the temperature range from 200 to 1000 °C.

upon thermal treatment of both unwashed and washed SAB when mixed with PVC at stoichiometric ratio (see Table 2). Thermal treatment was performed under inert conditions over a temperature range from 200 to 1000 °C. For data treatment, the species considered for discussion were those when the maximum equilibrium amount of the species was more than 0.1 g. The species reported here are those related to zinc, manganese, and iron.

It should be pointed out that the washing of SAB will result in dissolving hydroxides (KOH and NaOH) as well as any chlorides present (KCl). The presence of these species, as will be seen later, will result in formation of complex chloride species that would hinder the separation of zinc species in easy recoverable form. Therefore, the comparison between washed and unwashed SAB will highlight the impact of these species on the thermal treatment product.

3.2.1. *Zinc predicted species*

The effects of temperature and washing on the types and quantities of zinc species formed during thermal treatment of SAB-PVC mixture under inert atmosphere are shown in Fig. 2. For UW-SAB-PVC, the major solid zinc species formed are zinc chloride ($ZnCl_2$), di-sodium zinc chloride (Na_2ZnCl_4), sodium zinc chloride ($NaZnCl_3$), potassium di-zinc chloride (KZn_2Cl_5), and potassium zinc chloride ($KZnCl_3$). Traces of zincite are formed in the temperature window of 590-620 °C. The formation of these complex chlorides can be assigned to the reaction of the formed zinc chloride with NaCl and KCl to form sodium and potassium zinc chlorides. Any excess zinc chloride remains as $ZnCl_{2(s)}$, which then melts above a temperature of 310 °C, after which it starts steadily evaporating into gaseous zinc chloride. Di-sodium zinc chloride is stable up to a temperature of 500 °C, then it starts to decompose into zinc chloride, which is in liquid form at this temperature, while the sodium from this species starts reacting with manganese chloride ($MnCl_2$) to form sodium tetra-manganese chloride ($NaMn_4Cl_9$) (See Fig. 3A), whereas, potassium di-zinc chloride (KZn_2Cl_5) starts to decompose into liquid zinc chloride ($ZnCl_{2(l)}$) and gaseous $KZnCl_3$ at a temperature of 560 °C and disappears above a temperature of 580 °C. Part of the potassium from (KZn_2Cl_5) reacts with $MnCl_2$ to form $KMnCl_{3(s)}$. The gaseous zinc chloride increases steadily as a result of $ZnCl_{2(l)}$ evaporation and is also formed from the decomposition of solid $Na_2ZnCl_{4(s)}$ and $KZn_2Cl_{5(s)}$ up to a temperature of 630 °C then steadily decreases, while the amount of $KZnCl_3$ increases. Formation of small quantities of gaseous $NaZnCl_{3(g)}$ also takes place and keeps on increasing until a temperature of 800 °C is reached.

Small quantities of ZnO form in a narrow temperature window (590-620 °C) which then transforms into gaseous $ZnCl_2$. Additionally, small quantities of gaseous elemental zinc are observed to form above 770 °C

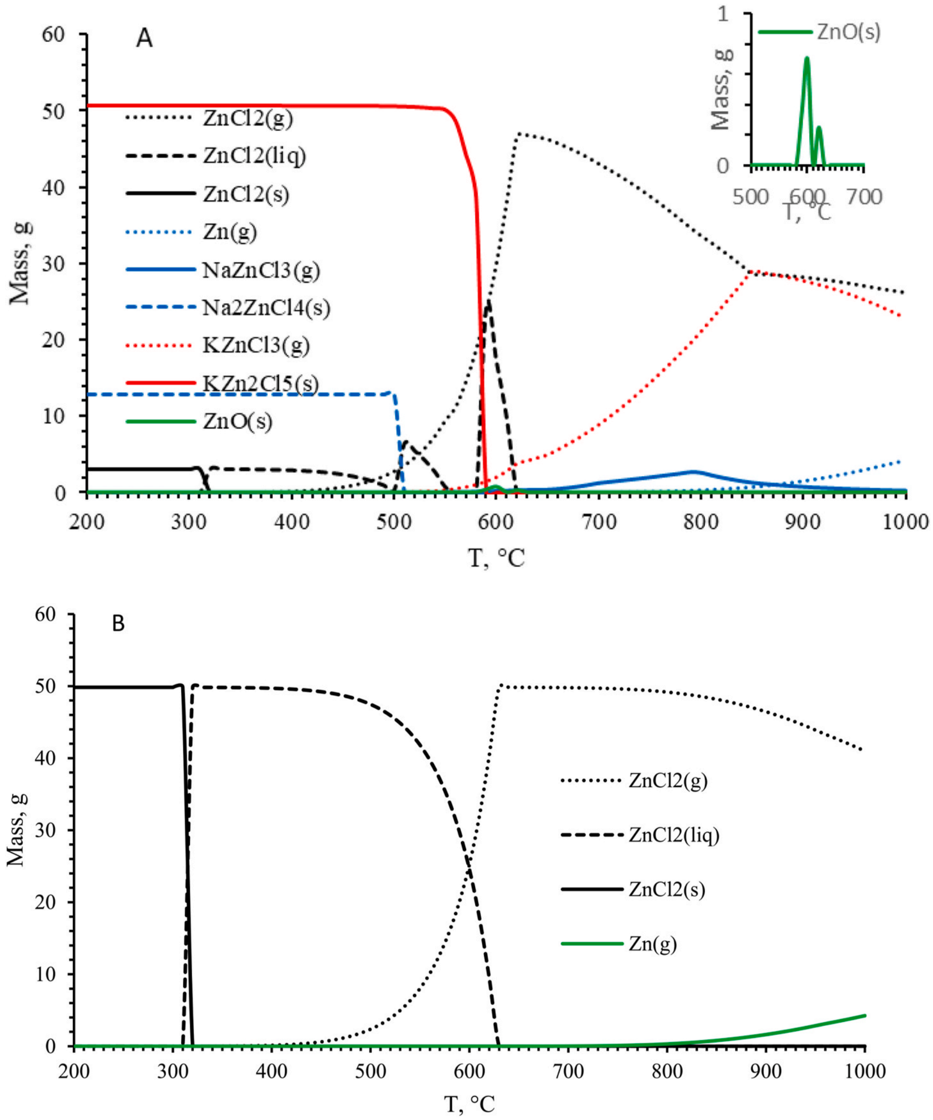

Fig. 2. Equilibrium amounts of zinc containing species for (A) UW-SAB-PVC and (B) W-SAB-PVC mixtures under inert atmosphere in the temperature range from 200 to 1000 °C.

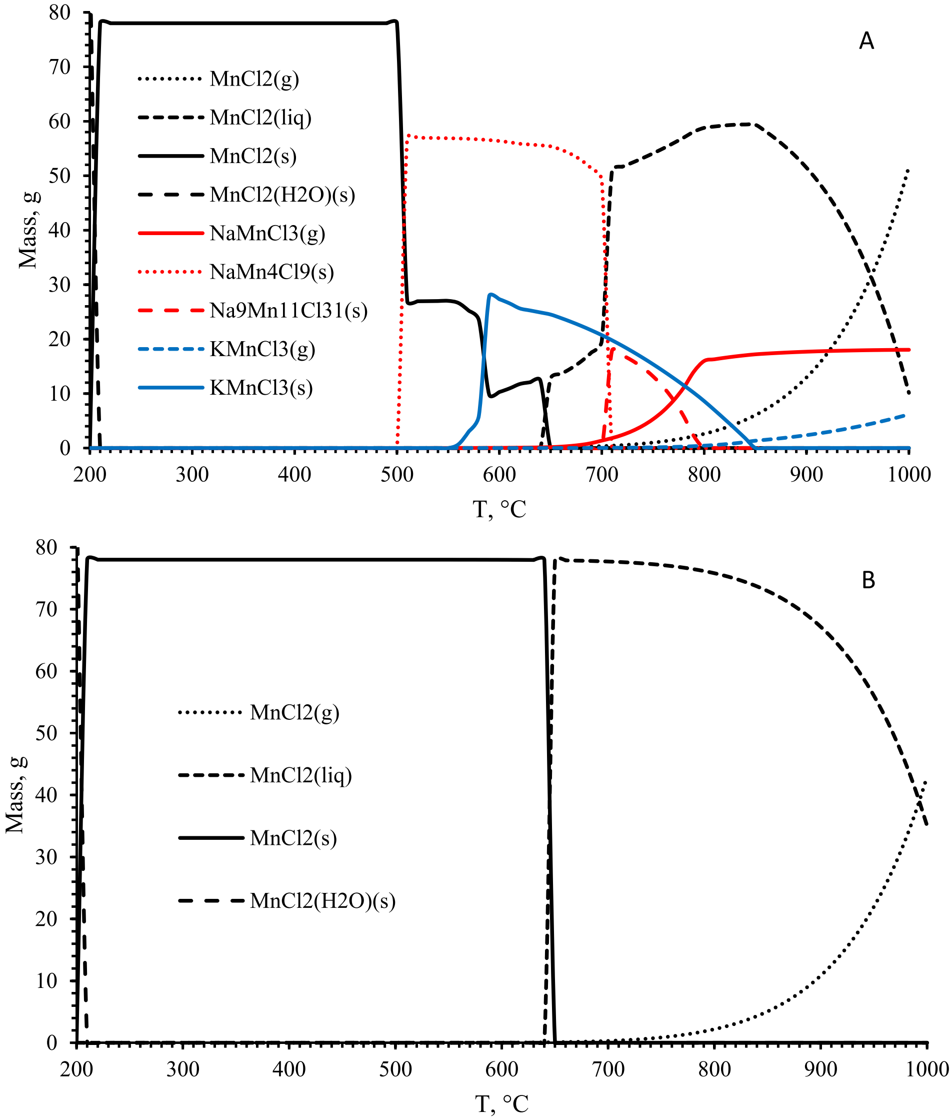

Fig. 3. Equilibrium amounts of manganese containing species for (A) UW-SAB-PVC and (B) W-SAB-PVC mixtures under inert atmosphere in the temperature range from 200 to 1000 °C.

as a result of $ZnCl_2$ reduction by carbon present in the SAB and that formed from the decomposition of PVC (see carbon profile in Fig. 5) .

However, when SAB is washed then thermally treated with a stoichiometric amount of PVC, the profile of zinc species becomes less complicated containing only $ZnCl_{2(s)}$, which melts at about 310 °C and completely converts into gaseous phase at a temperature of 630 °C, part of which is reduced into metallic gaseous zinc above 710 °C by carbon present in the SAB and that formed from the decomposition of PVC.

This important finding suggests that for W-SAB-PVC mixture, it is easy to obtain complete recovery of $ZnCl_2$ by water leaching if the thermal treatment is performed at temperatures below 300 °C followed by cooling to room temperature and leaching of the thermal treatment residue with water [37–40]. The other option is to perform the thermal treatment up to a temperature of 630 °C; at this temperature gaseous zinc chloride can be collected by condensation. More conclusive options will be revealed after discussing the manganese and iron behaviour in the sections that follow.

3.2.2. Manganese predicted species

The effects of temperature and washing on the types and quantities of manganese species formed during thermal treatment of SAB-PVC mixture under inert atmosphere are shown in Fig. 3. Below 200 °C, manganese chloride hydrate forms ($MnCl_2.H_2O_{(s)}$), which dehydrates into $MnCl_{2(s)}$ above this temperature. It remains stable up to a temperature of 510 °C where it begins to react with sodium from Na_2ZnCl_4 (see Fig. 2) to form sodium tetra-manganese chloride ($NaMn_4Cl_{9(s)}$), then reacts with potassium from KZn_2Cl_5 to form $KMnCl_3$ in the temperature range from 560 to 590 °C. Residual $MnCl_{2(s)}$ melts at a temperature of 640 °C. Above a temperature of 590 °C, $KMnCl_3$ starts to decompose into $MnCl_2$ and its potassium reacts back with $ZnCl_2$ to form gaseous $KZnCl_3$ (see Fig. 2). At a temperature of about 710 °C, all $NaMn_4Cl_{19(s)}$ decomposes into liquid $MnCl_2$ and $Na_9Mn_{11}Cl_{31}$, the latter then steadily decomposes into gaseous $NaMnCl_3$ reaching complete decomposition at a temperature of about 800 °C. $KMnCl_{3(s)}$ begins to decompose into $MnCl_2$, initially in solid form then transforms into liquid, reaching complete decomposition at a temperature of about 850 °C. Gaseous manganese chloride starts to appear at a temperature of 650 °C, while gaseous $KMnCl_3$ starts to appear at a temperature of 750 °C.

When SAB is washed and thermally treated with the stoichiometric amount of PVC, a simpler profile of manganese species is obtained whereby only $MnCl_2.H_2O_{(s)}$ forms which dehydrates into $MnCl_{2(s)}$ at a temperature of 200 °C. $MnCl_{2(s)}$ then melts at a temperature of about

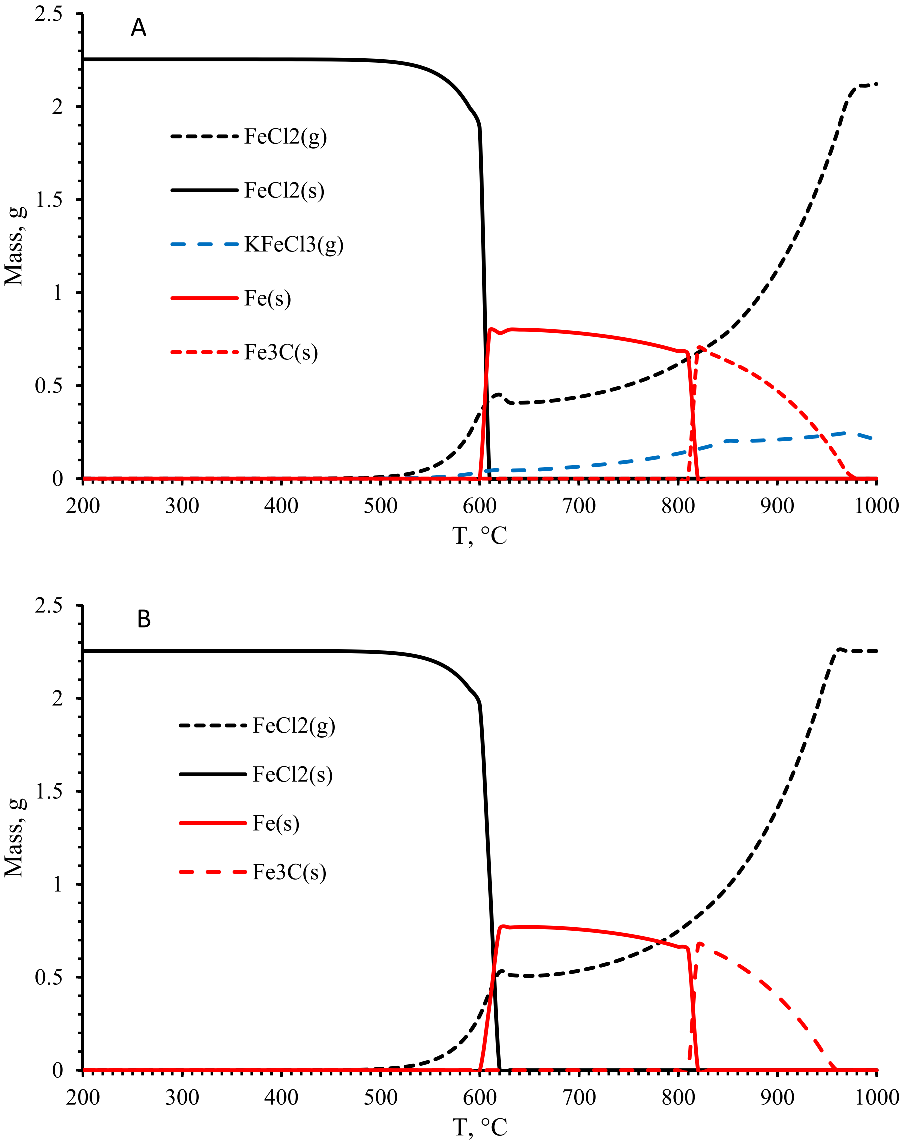

Fig. 4. Equilibrium amounts of iron containing species for (A) UW-SAB-PVC and (B) W-SAB-PVC mixtures under inert atmosphere in the temperature range from 200 to 1000 °C.

640 °C and completely converts into gaseous phase $MnCl_{2(g)}$ at a temperature of 1100 °C (not shown in the graph).

Likewise, a less complicated series of reactions takes place for the washed reaction mixture eliminating the effects of KOH, NaOH, and KCl. The important finding reported here suggests that for W-SAB-PVC mixture, it is possible to achieve a complete recovery of $ZnCl_2$ and $MnCl_2$ by means of water leaching of the post pyrolysis residue. Moreover, only a relatively low temperature of 300 °C followed by cooling to room temperature is needed to produce such a mixture (chloride water soluble mixture) [37–40]. The other option is to perform the thermal treatment up to a temperature of 630 °C; at this temperature gaseous zinc chloride can be collected by condensation. However, manganese will remain as solid manganese chloride; if the residue is cooled to room temperature and leached in water, manganese can be collected as aqueous manganese chloride. Using this procedure, one can obtain complete separation and recovery of both zinc and manganese.

3.2.3. *Iron predicted species*

The effect of temperature and washing on the types and quantities of the formed iron species during thermal treatment of SAB-PVC mixture are presented in Fig. 4. Below a temperature of 500 °C, iron chloride appears mainly in solid form which slowly evaporates up to a temperature of 600 °C. At this temperature, all remaining solid iron chloride is reduced into elemental metallic iron by carbon present in the SAB and that formed from the decomposition of PVC. Above 600 °C small part of iron is consumed to form $FeCl_{2(g)}$ and $KFeCl_{3(g)}$ up to a temperature of 820 °C, where the remaining iron converts to cementite (Fe_3C). Above 820 °C, cementite converts mainly into gaseous $FeCl_{2(g)}$, reaching complete conversion at a temperature of 980 °C and only very few converts into $KFeCl_{3(g)}$.

When SAB is washed then thermally treated with the stoichiometric amount of PVC, the profile of iron species remains the same as that obtained for unwashed SAB with the exception that $KFeCl_3$ is not formed.

3.2.4. *Carbon, water and HCl predicted species*

The effects of temperature and washing on the types and quantities of carbon species, water and residual unreacted HCl formed during thermal treatment of SAB-PVC mixture under inert atmosphere are shown in Fig. 5. The HCl profile shows that there is about 5 g excess. This suggests that the amount of PVC used in the mixture can be reduced by about 6%. As for carbon, initially, it reacts with water and CH_4 to form CO_2 and

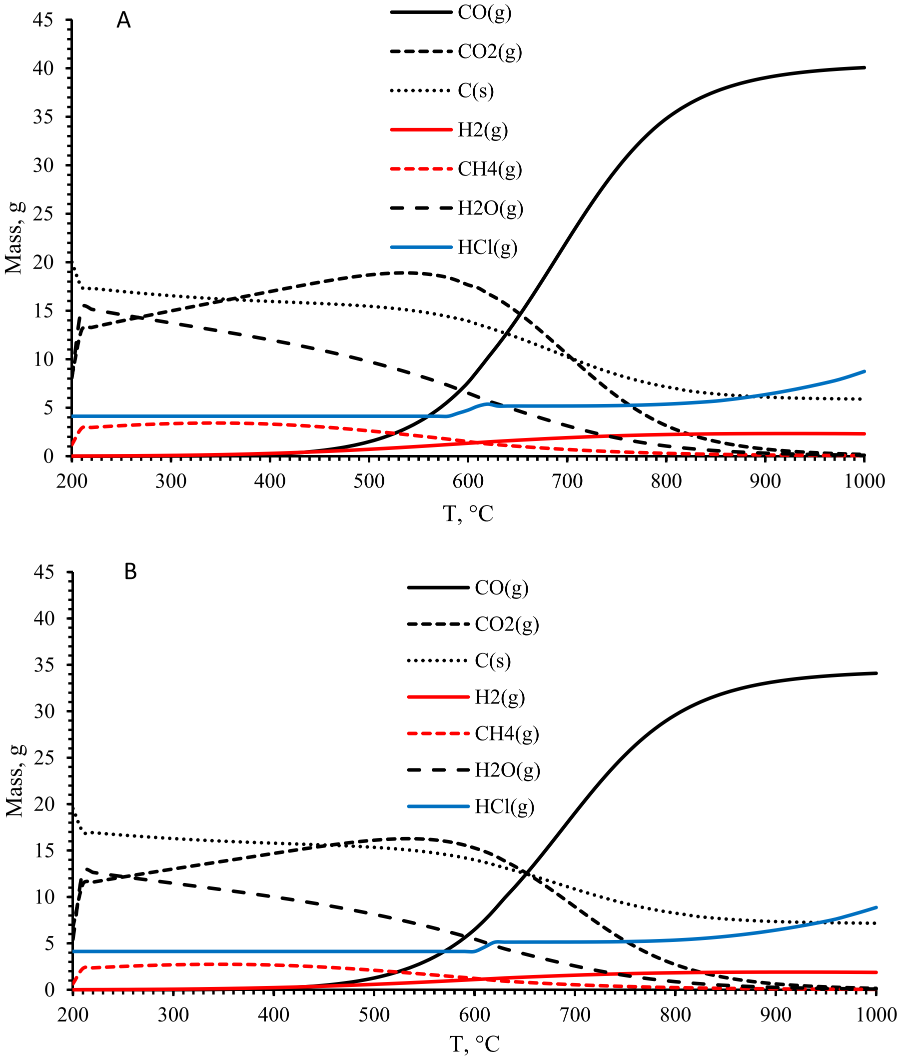

Fig. 5. Equilibrium amounts of carbon containing species, water and HCl for (A) UW-SAB-PVC and (B) W-SAB-PVC mixtures under inert atmosphere in the temperature range from 200 to 1000 °C.

hydrogen, up to a temperature of about 550 °C, then CO_2 reacts with C to form CO back. The observed increase in HCl at a temperature of about 600 °C could be related to the formation of metallic iron.

When SAB is washed then thermally treated with stoichiometric amount of PVC, the profile of carbon species, water and residual unreacted HCl remains the same as that obtained with unwashed SAB with slight change in the amount of these species.

3.2.5. *Recovery of Zn, Mn, and Fe gaseous species*

Fig. 6 shows the effects of temperature and washing on the types and quantities of gaseous metallic species formed during thermal treatment of SAB-PVC mixture under inert atmosphere.

For unwashed SAB, it is evident that separation of valuable species ($ZnCl_2$ and $MnCl_2$) is difficult by evaporative separation with exception of separating $ZnCl_2$ below 620 °C, however, it would be contaminated with $NaZnCl_3$.

However, for washed SAB, the separation of $ZnCl_2$ could be possible at a temperature below 620 °C; at this temperature slight contamination with $FeCl_2$ can be experienced.

3.2.6. *Post water leaching of SAB-PVC pyrolysis residue*

The pyrolysis residues from washed and unwashed SAB-PVC mixture were tested for metal extraction using water leaching. The dissolution of the chlorides in water and the calculated thermodynamic data were based on the following reactions:

$ZnCl_{2(s)} = Zn^{2+} + 2Cl^{-}$ Reaction 8

$MnCl_{2(s)} = Mn^{2+} + 2Cl^{-}$ Reaction 9

$FeCl_{2(s)} = Fe^{2+} + 2Cl^{-}$ Reaction 10

$Na_2ZnCl_4 = 2Na^{+} + Zn^{2+} + 4Cl^{-}$ Reaction 11

$KZn_2Cl_5 = K^{+} + 2Zn^{2+} + 5Cl^{-}$ Reaction 12

The behavior of Zn, Mn, and Fe species (aqueous and solid) with respect to the pH of the leaching solutions for both washed and unwashed SAB-PVC pyrolysis residues are presented in Fig. 7 A, B, C and D.

The behavior of zinc, manganese, and iron in the leaching solution for both washed and unwashed SAB remained almost similar. At a pH of ≤6.0, all the components are dissolved in the leaching solution (i.e., fully recovered). However, in the pH range 6 – 8 zinc hydroxychloride ($Zn_5(OH)_8Cl_{2(s)}$) phase precipitates reaching a maximum at a pH of 7.5 before transforming completely into zincite (ZnO) phase at a pH of 8. When ZnO forms, the dissolved Zn drops to below 0.23% and 0.26%, for washed and unwashed mixtures, respectively. At a pH = 8.0, it can be noticed that manganese is still completely dissolved, suggesting that in a well-controlled pH solution, a good degree of separation between zinc

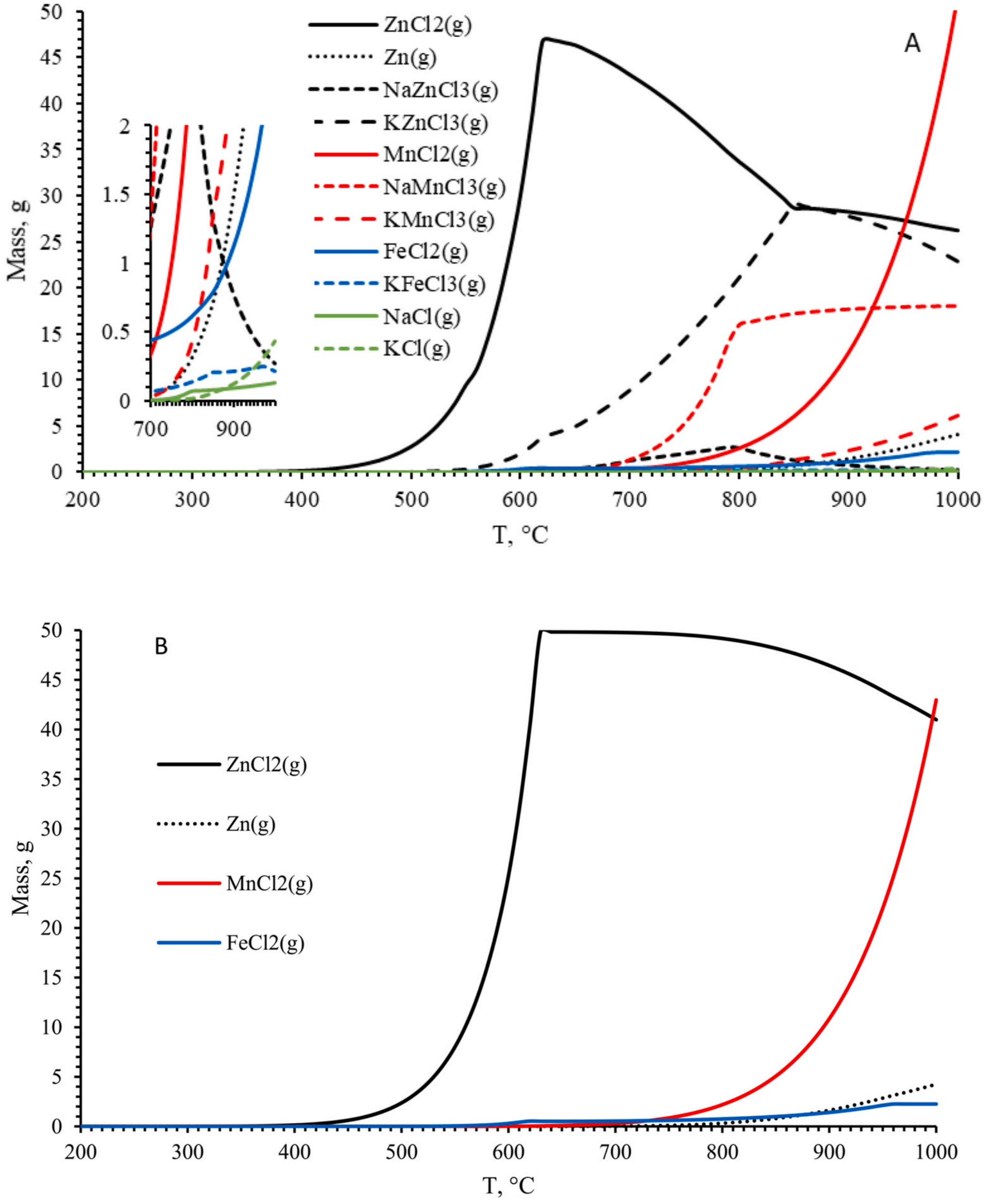

Fig. 6. Equilibrium amounts of gaseous metallic species for (A) UW-SAB-PVC and (B) W-SAB-PVC mixtures under inert atmosphere in the temperature range from 200 to 1000 °C.

and manganese can possibly be obtained. As the pH increases further ($8.5 \leq$ pH), manganese starts precipitating in the form of Mn_3O_4. More Mn_3O_4 is precipitated with increasing pH until 0% of Mn^{2+} is present in the solution in the pH range 10.5 – 14 for both washed and unwashed SAB. Zinc, on the other hand, keeps precipitating until a pH of 10.5 is reached after which it starts dissolving slowly again and then dissolves abruptly and completely at a pH of 14.0. It can also be seen that iron precipitates almost entirely in the pH range 9.0 – 13.0 as $Fe(OH)_{2(s)}$.

The major difference between the leaching of washed and unwashed pyrolysis residues is the contamination of the unwashed residue leaching solution with K^+ and Na^+ ions. The precipitation of these ions in the forms of NaOH and KOH takes place at high pH values of ≤ 9.5 and ≤ 13 for Na^+ and K^+, respectively (see Fig. 7). This, in turn, can potentially complicate the separation of zinc and manganese by electrowinning.

3.2.7. Recommendations for the thermal treatment of SAB-PVC mixture

Based on the discussion of the thermodynamic simulations above, the best route for the treatment of SABs with PVC waste can be summarized as follows:

1. SAB should initially be washed with water to remove KOH, NaOH and KCl.
2. The washed SAB is then mixed with stoichiometric amount of PVC (see Table 2).
3. Perform the thermal treatment of the W-SAB-PVC mixture under an inert atmosphere up to a temperature of 300 °C.
4. Cool the pyrolysis residue of the W-SAB-PVC to room temperature.
5. Leach the residue in water with a pH of 5 – 6. At this pH, all $ZnCl_2$ and $MnCl_2$ should be dissolved.

4. Conclusions

In this work, a thermodynamic assessment of the thermal treatment of PVC mixed SAB at a stoichiometric ratio was performed. Zinc and manganese bearing oxides showed an excellent chlorine fixation leading to the transformation of these oxides into their chloride counterparts. At

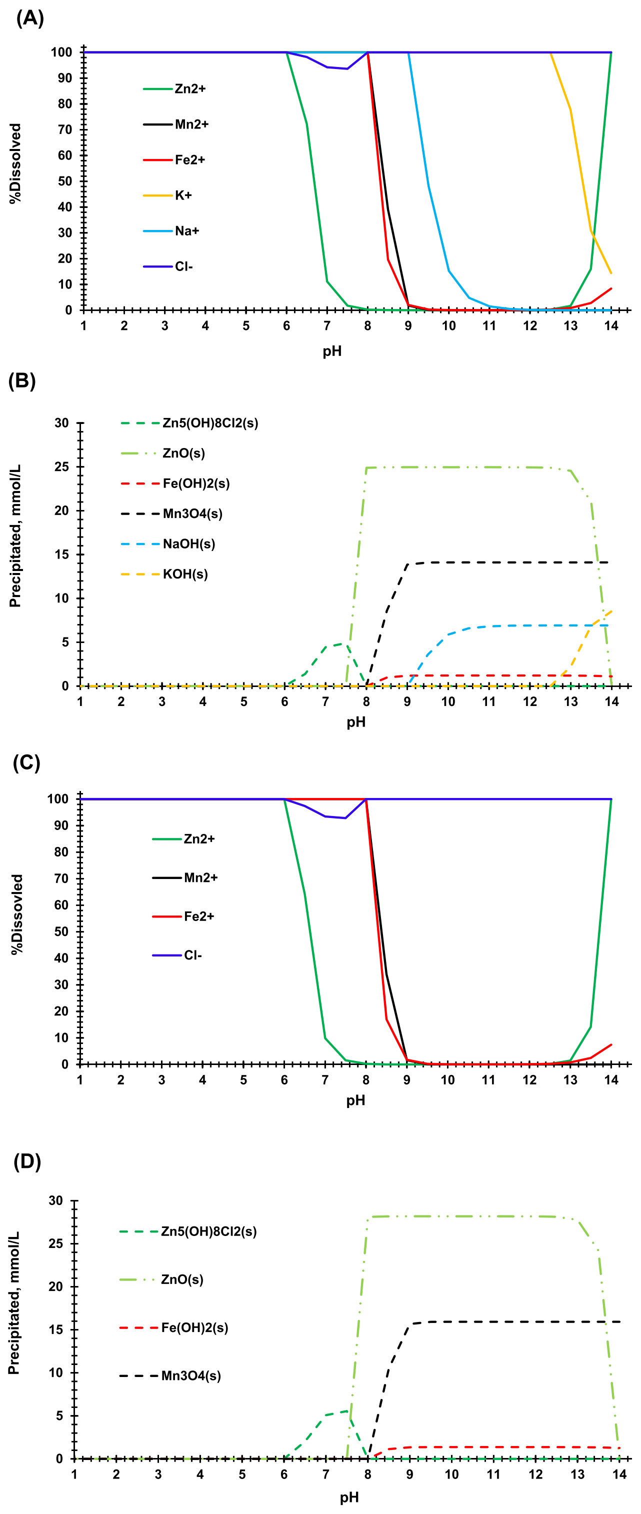

Fig. 7. Speciation of leached components in water for the post pyrolysis residue of unwashed (A and B) and washed (C and D) SAB-PVC mixtures at a temperature of 25 °C and a solid to liquid ratio of 1g:100mL.

a pyrolysis temperature equal to 300 °C, it is believed that the generated residue should contain zinc and manganese in their chloride forms making it easy to extract them using water in the pH range 5-6. The washing of the SAB washed out NaOH, KOH, and KCl prior to the thermal treatment. This would suppress the recovery of sodium and potassium bearing compounds in the leaching solution which enhances the extraction selectivity of both zinc and manganese. Iron could not be completely isolated from the leaching solution due to the chlorination of Fe_2O_3 into $FeCl_2$ (after reduction by carbonaceous material). Hence, more research needs to be done on suppressing the dissolution of iron with both zinc and manganese either by altering the conditions of the thermal treatment or the leaching procedure.

CRediT authorship contribution statement

Mohammad Al-Harahsheh: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Writing – original draft, Writing – review & editing. **Sanad Altarawneh:** Data curation, Formal analysis, Investigation, Software, Writing – review & editing.

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

Data will be made available on request.

Acknowledgment

The authors would like to thank Jordan University of Science and Technology for supporting Prof. Mohammad Al-Harahsheh during his sabbatical leave (Grant # 108/2019).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cscee.2023.100568.

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