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S-Cl-Na-K Chemistry During MSW Gasification: a Thermodynamic Study

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This succinct thermodynamic study addresses the gasification chemistry (air/fuel ratio of 0.5) of four chemical elements involved in ash-related challenges, i.e. Na, K, S and Cl. At typical temperatures for the process studied, the following main trends have been observed: (1) the phase distribution of these elements may change abruptly, i.e. within a narrow temperature range; (2) the main practical outcome of point 1 is that it will be difficult to optimise a given process giving the versatility of chemistry vs temperature but stable operating conditions are preferable. Methods exist to abate ash-related challenges but their selection should include both practical and economic considerations.

1. Introduction

Using Municipal Solid Waste (MSW) as an energy source (aka WtE - Waste-to-Energy or EfW - Energy from Waste), with a significant fraction being of biogenic origin and therewith renewable, is a well-established practice in several EU countries as well as parts of Asia and North America. The most common technological solution is combustion on a moving grate with heat and/or power production. However, according to Eurostat (2014), 34 % of EU-28 MSW were neither material- nor energy-recovered but landfilled in 2012. As illustrated by the EU Waste Hierarchy, WtE is, combined with material recycling and biological treatment, an efficient and well-regulated waste management alternative, but sometimes suffers from a negative public perception. In this context, innovative thermal solutions, such as MSW gasification may both avoid such pitfalls as well as offer additional advantages.

However, gasification is not exempt from operational challenges with ash-related ones (corrosion, fouling, slagging) being of prime importance. These challenges have an impact on the plant overall performance and hence profitability.

Using Energos technology operational as case study, this article proposes a thermodynamic study on the chemistry of selected ash-forming elements (alkalis, i.e. Sodium Na and Potassium K), Sulphur (S) and Chlorine (Cl) during gasification (air/fuel ratio of 0.5) as they are central in the aforementioned ash-related challenges. Energos technology is a grate-based MSW gasification concept. The principle is a two-stage process where gasification (syngas production) is directly followed by combustion of the syngas to produce heat/power. Several Energos plants are currently in commercial operation or under procurement/construction.

Little attention has been given to alkalis at reducing conditions in thermal (gasification) systems, except for a few studies such as Konttinen et al. (2005) with Solid Recovered Fuel (SRF) as a fuel; Becidan and Sørum(2010a) investigating biomass and Hau et al. (2008) focusing on solid waste. During combustion, various transformations are taking place involving ash compounds (Wiinikka, 2005) and reducing conditions may affect both speciation and phase distribution. To optimize plant operation and develop gasification models, it is important to understand both the fluid dynamics and thermal processes. A first beneficial step to better comprehend the latter is the use of thermodynamic equilibrium methods. Thermodynamic equilibrium

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calculations have proven their relevance in a variety of applications and despite known limitations (see 2. Methodology) they provide valuable information on chemical trends. Such calculations are a powerful tool and, at present, represent the most practical computational possibility for investigating elemental chemistry in a multicomponent and multi-phase complex thermal system. This study presents the Na-K-S-Cl-containing products and chemical trends at varying temperature with focus on the formation of corrosive compounds during MSW gasification.

2. Methodology (thermodynamic model)

Thermodynamic equilibrium calculations are also known as global equilibrium analysis (GEA) and are solely based on the minimization of Gibbs free energy using the thermodynamic data for all phases and compounds included in a user-defined database. For studying thermal processes, the elemental composition of the fuel and of the gas atmosphere at given temperatures and pressures are the required inputs.

The limitations of this method are well-known (temperature/concentration gradient, kinetics, fuel elemental speciation or physical/transport processes are not considered). However, adequately designed methodologies bring valuable information on overall stabilities and speciation trends.

In this study the calculations are made using the FactSage 6.3 software package with a custom-made database based on commercial databases (the FACT and SGTE databases). The database considers:

- 1 gas phase with 621 species; 3 pure liquid phases; 678 pure solid phases
- 1 liquid slag phase (oxide/silicate phase) including K_2O, Na_2O, CaO, MgO, Al_2O_3, $NaAlO_2$, SiO_2, FeO, Fe_2O_3, PbO, ZnO, MnO
- 1 molten salt phase including NaCl, KCl, NaOH, KOH, Na_2SO_4, K_2SO_4, Na_2CO_3, K_2CO_3, Na_2S, K_2S
- 7 Solid solutions: Na_2SO_4-K_2SO_4-Na_2CO_3-K_2CO_3-Na_2S-K_2S; Na_2SO_4-K_2SO_4-Na_2CO_3-K_2CO_3; Non-stoichiometric $K_3Na(SO_4)_2$; Na_2S-K_2S; NaCl-KCl; NaBr-KBr; NaF-KF

3. Case study (the fuel, the operational data and the calculation parameters)

The calculation parameters are that of a WtE plant using the Energos technology (Houshfar et al., 2013).The fuel data are also from an Energos plant (Table 1). Ash chemistry associated with alkalis (Na, K), Cl and S chemistry is the focus of these calculations. The operational parameters are 600-1500 °C (one calculation point every 100 °C) with an air/fuel ratio of 0.5. In addition, the following assumptions have been made: (1) the fuel moisture is not included in the calculations as it is removed before devolatilisation starts; (2) several ash-forming elements are less reactive than assumed by the thermodymanic data. In consequence, only 5 % of the most inert elements (Al, Si and Fe) are included in the calculations; (3) Nitrogen (N) only forms N_2.

Table 1: Composition of the fuel (MSW): main species of interest

Elements	Wt% (dry basis)
C	47.22
H	6.39
O	28.43
N	1.76
S	0.20
Cl	0.63
Ash*	15.37
Na	0.47
K	0.43

* Elements included in the calculations but not discussed in this article: Al, As, Ca, Cd, Cr, Cu, F, Fe, Hg, Mg, Mn, Ni, Pb, P, Si, Ti, Zn.

4. Results and discussion

4.1 Sodium (Na)

The main trends and features predicted by thermodynamic calculations for Na chemistry are:

- Two compounds are important at the temperatures studied: Na_3PO_4 (solid) and NaCl (gas)
- A Na-containing liquid slag (oxide/silicate phase) appears above 1000/1200 °C
- Some {NaCl – KCl} melt phase is predicted at low temperatures (700-800 °C)
- Na (gas) is predicted at high temperatures (above 1200 °C)
- Na phase distribution and speciation is significantly affected by temperature (see Figure 1)

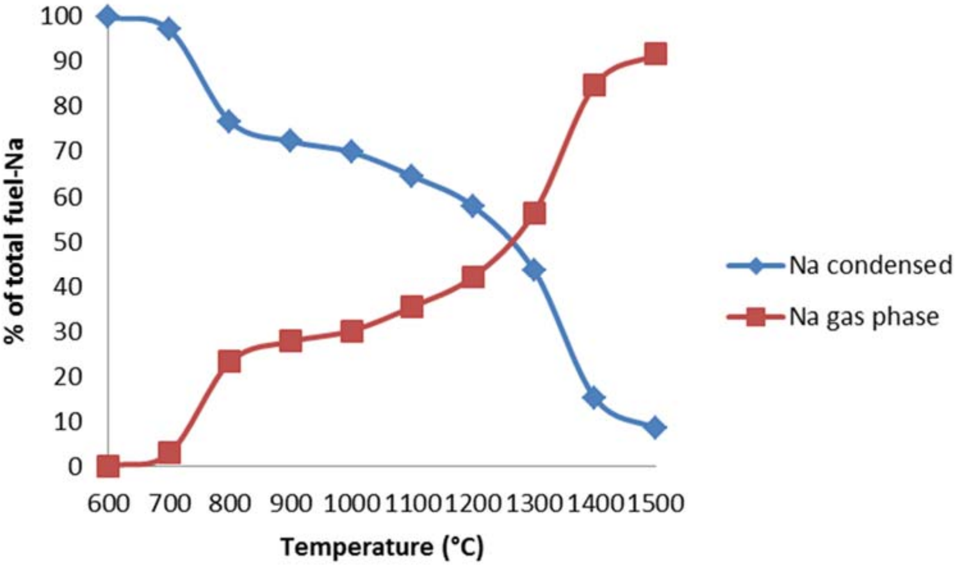

Figure 1. Phase distribution of Na

The main implication of the predicted Na behaviour for plant operation is the fact that a significant portion of Na forms corrosive gaseous chlorides. In addition, the results show that modest changes in temperature on the grate may have a significant influence on Na chemistry, both speciation and phase distribution. This behaviour makes it difficult to implement a single measure to efficiently abate Na-associated challenges (corrosion, etc.).

The enrichment of P in the solid residues (both bottom and fly ash) during combustion has been observed in other thermal processes using P-rich fuels such as sewage sludge (Pettersson et al., 2008). Considering the importance of P as a plant nutrient and its upcoming scarcity, this offers a possibility for additional revenue for WtE plants if efficient and affordable extraction processes can be designed.

A liquid slag is predicted, mainly at high temperatures, representing above 10 % of fuel-Na at 1100-1500 °C. The degree of slagging taking place in the primary chamber affects the temperature field which in turn affects overall slagging (Tchobanoglous and Kreith, 2002). Higher flame temperatures and hot spots caused by the slag will increase the total amount of (alkali) metals released, hence contributing to fouling and deposit-induced corrosion. Furthermore, melt phases may promote several corrosion reactions (Bugge et al., 2007).

4.2 Potassium (K)

K is found in a similar concentration (weight basis) as Na in the fuel studied. The presence of two rather than only one alkali (such as in most biomass feedstocks) may have various consequences on chemistry, including increased risk of formation of gaseous alkali chlorides if enough Cl is available and competition between the two alkali metals for selected elements as they have similar chemical affinities. The predicted K chemistry (Figures 2 and 3) can be described as such:

- Gaseous corrosive KCl represents more than 50 % and up to about 80 % of fuel-K from 800 °C
- Solid K_3PO_4 is an important compound for K chemistry between 600 and 900 °C
- An oxide slag is predicted over the whole temperature range encompassing 8-20 % of fuel-K
- The phase distribution of K is significantly affected by temperature. The speciation shift is more abrupt than for Na: while over 94 % of K is in the condensed phase at 600-700 °C (as chloride, phosphate and oxide slag), this proportion has dropped to about 50 % at 800 °C

K and Na exhibit similar chemical trends but with distinctive features, the main ones being that K has higher affinities with Cl than Na; this also explains why K is more volatile than Na at higher temperatures. This is in good accordance with previous work (Becidan et al., 2010b).

The behaviour of K shows that it is a major corrosion vessel as it transports Cl from the primary chamber and therewith facilitates high-temperature Cl-induced corrosion on various metal surfaces, a major issue for WtE plants. Roughly 25-30 % of the maintenance costs are spent on the parts (superheater bundles, etc.) especially exposed to corrosion. The presence of a K-containing slag over this temperature range is also an added challenge, as commented for Na.

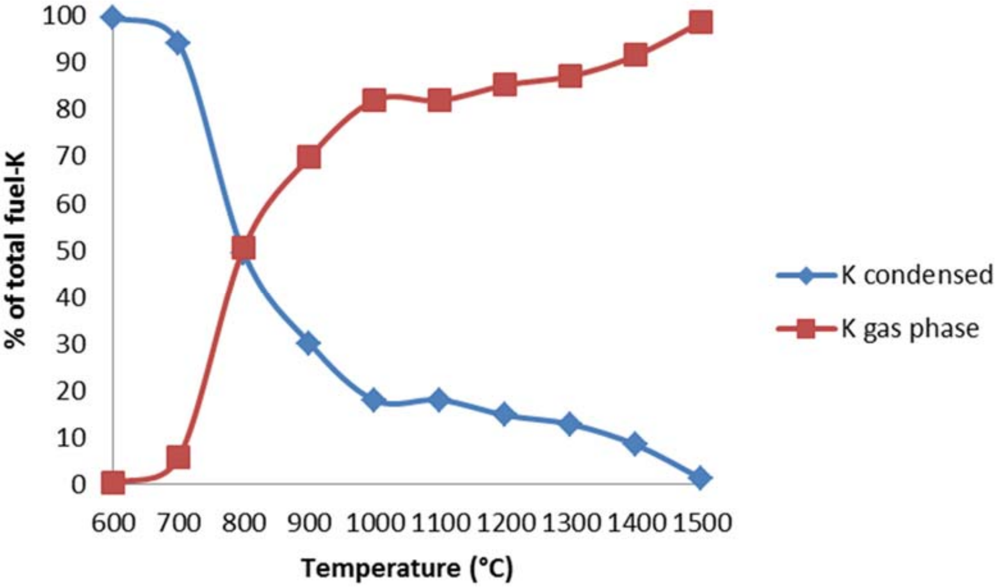

Figure 2. Phase distribution of K

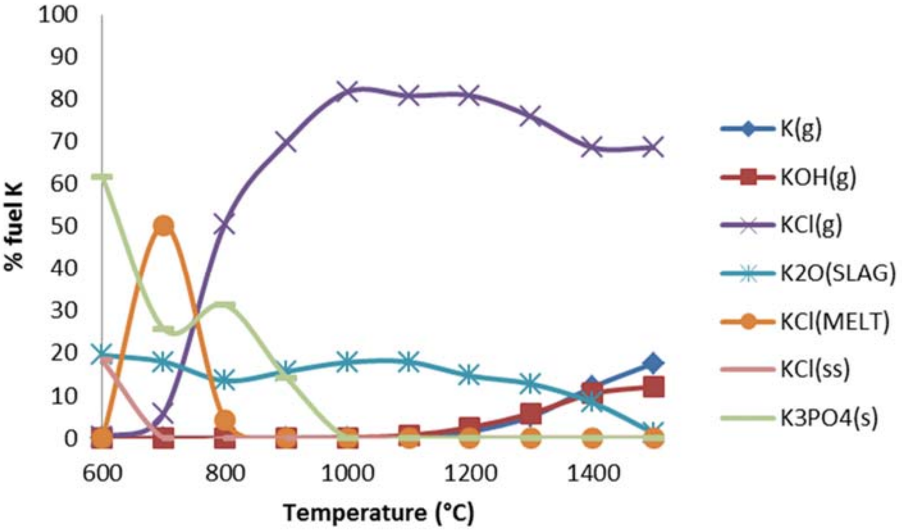

Figure 3. Speciation of K. g: gas; MELT: melt; SLAG: slag; s: solid; ss: solid solution

4.3 Sulphur (S) & Chlorine (Cl)

In combustion systems, a significant proportion of S is forming sulphates and competes with chlorine to react with alkalis (Na, K). Alkali sulphates are not corrosive (under most conditions) and are therefore preferable to chlorides. Sulphates are even used as additives to reduce corrosion in combustion systems such as with the ChlorOut system patented by Vattenfall. The modus operandi and efficiency of sulphates has been widely proven and discussed (Becidan et al., 2009). However, under sub-stoichiometric conditions such as gasification, sulphates are not formed in significant amounts. Sulphur has a stable chemistry over the whole range studied with H_2S (gas) being the main component (with 73-90 % of fuel-S). Hydrogen sulphide is an undesirable product as it is corrosive and destroys metal surfaces by forming FeS (Bugge et al., 2007).

Cl behaviour follows two distinct trends (see Figure 4): a low temperature one (600-700/800 °C) and a high temperature one (700/800-1500 °C). At low temperatures, chlorine can be found in the condensed phase as corrosive alkali chlorides. At high temperatures, the three main compounds are all in the gas phase. They are HCl, KCl and NaCl. Interesting results can be observed: (a) the average proportion of the two alkali chlorides at 800-1500 °C are similar and increasing with temperature until reaching a plateau/slightly decreasing; (b) HCl (g) is decreasing with temperature until 1400 °C from its maximum value of about 35 % of fuel-Cl at 800 °C.

Cl speciation brings supplementary information in addition to alkali chemistry concerning Cl-induced high temperature corrosion. The overwhelming majority (more than 90 %) of Cl will form corrosive gaseous alkali chlorides at typical combustion/gasification temperatures. It appears therefore unavoidable that in this case study, almost all the available Cl will be corrosive and will be transported to various hot metal surfaces either as a gas or by condensing onto particles that may in turn deposit on metal surfaces.

4.4 Measures to abate ash/alkali & Cl/S related challenges

Mitigating ash-related challenges (fouling, slagging, corrosion) is an arduous task and unambiguous results are seldom, given the complex multi-element chemistry and physical processes at play. Several methodologies (at various states of maturity) are available: (1) Additives, including "smart" mixtures. Aluminosilicates can prevent the formation of corrosive alkali chlorides that are replaced by alkali aluminosilicates that remain in the bottom ash, are inert and have a high melting point (Wang et al., 2014); (2) Process optimisation including design (air distribution, superheater parameters, etc.); (3) Extensive fuel characterisation to assess quality, pre-treatment and system requirements; (4) Boiler cleaning (sonic, explosive); (5) Materials development (corrosion resistant alloys, coatings); (6) Advanced systems (Oxygen Enhanced Combustion, etc.) including gasification and pyrolysis; (7) Prediction (modelling). Other factors are interesting when considering ash-related challenges, i.e. heterogeneity/local conditions (concerning fuel properties and O distribution especially, as shown in Becidan et al., 2010b) as well as the fate of specific trace metals (Pb, Zn).

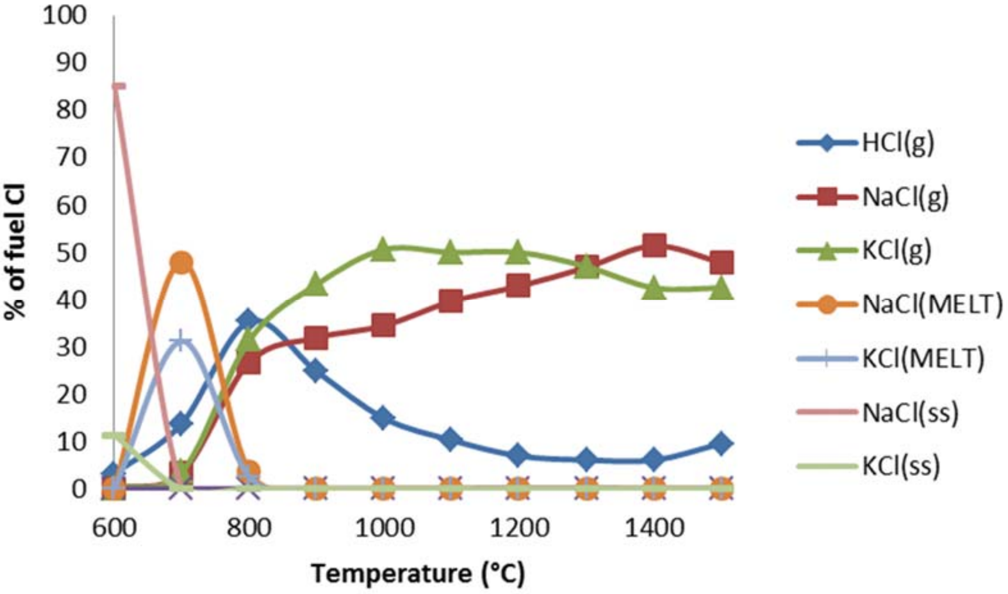

Figure 4. Cl speciation during gasification of MSW. g: gas; MELT: melt; ss: solid solution

5. Conclusions

This succinct thermodynamic study addresses the waste gasification chemistry (air/fuel ratio of 0.5) of four chemical elements involved in ash-related challenges, i.e. Na, K, S and Cl. At typical temperatures for the process studied, the main trend observed is that the phase distribution of these elements may change abruptly, i.e. within a narrow temperature range. The main practical outcome is that it will be difficult to optimise a given process giving the versatility of chemistry with temperature. However, stable operating conditions are preferable. Different approaches exist to abate ash-related challenges, but selecting one (or a combination) is complex and should be based on both practical and economic considerations.

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