



Research paper

Mobilisation of trace elements during thermal conversion of algae cultivated in ash dam water



Daniel J. Lane ^{a,*}, Philip J. van Eyk ^a, Rocky de Nys ^b, David A. Roberts ^b, Andrew J. Cole ^b, Peter J. Ashman ^a

^a School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

^b MACRO – the Centre for Macroalgal Resources and Biotechnology, College of Marine and Environmental Sciences, James Cook University, Townsville, Qld 4811, Australia

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ABSTRACT

The work presented here assesses the potential for the mobilisation of 11 trace elements (As, Be, Co, Cu, Mn, Ni, Pb, Sb, Se, V, Zn) during the thermal conversion of micro- and macroalgae that were cultivated in ash dam water. The volatility of the trace elements was quantified by mass balances based on elemental analyses of char and ash residues. The residues were prepared in a laboratory-scale fixed-bed reactor at a range of different temperatures (500–1100 °C) and gas atmospheres (N₂, 2% O₂ and CO₂) to simulate pyrolysis, combustion and gasification processes. The results showed high volatilities for Se (~79–97%) and As (~51–79%) below 500 °C. Zn, Pb and Sb were mainly volatilised above 700 °C. The different gas atmospheres had little influence on the volatility of these elements, which increased sharply to more than 90% with increasing temperature from 700 to 1100 °C. Volatilities for V, Mn, Cu, Co, Ni and Be were relatively minor over the full range of investigated operating conditions. Samples of each alga and their thermal conversion residues were subject to batch leaching in water. All of the tested trace elements, except for Pb and Be, were partially leached from the algae. Vanadium was up to 4–5 times more leachable in the combustion residues than in the algae. The other trace elements were generally less leachable following thermal conversion. The trace elements were more stable in residues prepared under pyrolysis and gasification conditions than in residues prepared under combustion conditions at the same temperature.

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1. Introduction

Vast volumes of waste water are generated at coal-fired power stations, particularly in countries like Australia where it is common practice to dispose of coal-ash in large ponds, known as ash dams. Ash dam water (ADW) often contains potentially harmful trace elements (TEs), which have been leached out of coal-ash, in concentrations that exceed water quality criteria [1]. In such cases the ADW cannot be safely discharged from the power station. Cost effective and environmentally sustainable technologies are critical to remediate ADW and render it reusable. A new technology being developed at the Centre for Macroalgal Resources and Biotechnology at James Cook University involves the integrated production of algae in ADW to sequester environmentally important TEs.

Recent studies [1,2] have demonstrated the production of algae in TE contaminated ADW from the Tarong power station in Queensland, Australia. The concentrations of most regulated TEs in the ADW were successfully reduced to levels that comply with Australian water quality standards [3]. However, effective utilisation of the produced algal biomass still remains a key challenge for the algal-based bioremediation concept.

Thermal conversion, by means of pyrolysis, combustion or gasification, is one possible use of the produced ADW algae that allows for heat and power generation. Much of the infrastructure required for heat and power generation is likely already available at the power station and the total volume of bio-solids is substantially reduced in the process which is beneficial from the point of waste management. However, there are potential risks in the case that the TEs sequestered by the algae become mobile. If released into the environment the TEs can accumulate at levels much higher than which they occur naturally [4] and cause significant harm to

* Corresponding author.

E-mail address: daniel.lane@adelaide.edu.au (D.J. Lane).

delicate ecosystems and to human health [5,6]. The different pathways for the TEs to make their way into the environment are shown schematically in Fig. 1. The TEs are introduced to the power station with the coal feed which is combusted in a boiler at high temperatures to produce heat and power for electricity generation. Bottom ash and fly ash are generated as by-products during this process. The fly ash is generally enriched in various TEs and is disposed of in an ash dam. The algae can be used to remediate the ADW in bioremediation ponds by sequestering TEs dissolved in the water via a two-phase process [7]. The first phase involves passive adsorption of the TE onto cell surfaces and the second phase involves transport of the TE across the cell wall and into the cytoplasm, where it can be stored in a non-toxic form [8]. The produced algae is harvested, dried and then used as a feedstock for thermal conversion (*i.e.* pyrolysis, combustion or gasification). During thermal conversion, the TEs can be released into the gas phase or be retained in the solid ash (or char) residues. Volatilised TEs risk being emitted from the stack and into the atmosphere. The TEs retained in the solid residues can undergo further fractionation if the residues are contacted with water. TEs leached from the residues can migrate to and contaminate ground and surface waters [9]. Roberts *et al.* studied the potential for TE leaching from ADW algal chars produced under slow pyrolysis conditions [2] and the transfer of TEs from the produced chars to edible crops and soil pore water [10]. Apart from this work, little has been done to assess the potential for TE mobilisation both during and post thermal conversion of ADW algae, particularly under conditions relevant to industrial heat and power applications.

The volatility of the TEs during thermal conversion has been studied for coal and for terrestrial biomass fuels by means of thermodynamic equilibrium calculations (TECs) [11–13], laboratory scale experiments [14,15] and ash sampling at full scale plants [16,17]. The ranges of volatilities reported in these studies vary widely for many of the TEs. Nevertheless some general trends are evident. Selenium is predominately volatilised at low temperatures (<500 °C), regardless of the gas atmosphere. As, Pb, Sb and Zn display intermediate volatilities. The volatility of these elements is highly sensitive to temperature and tends to be greater under

reducing gas atmospheres which are characteristic of gasification and pyrolysis processes. Co, Mn, Ni and V are more or less refractory below 1100 °C or are volatilised only to a minor extent. Studies that address the volatility of Cu are particularly conflicting. Some studies [18,19] report Cu to be mainly retained in the char and ash residues at temperatures below 1100 °C. Other studies [13,14] indicate that Cu is largely volatilised below 1100 °C. Available literature on the volatile behaviour of Be is limited [11,20]. Several authors [12,21,22] have emphasised that the extent of TE volatilisation depends on both fuel composition and on operating parameters such as temperature and gas atmosphere. The chemical composition of algae has been studied in previous work [23,24] and was found to differ in many ways from that of coal and commonly used terrestrial biomass fuels. Despite this, there has been limited work to determine the extent to which the TEs are volatilised from algae during thermal conversion or to understand how this varies for different temperatures and for different gas atmospheres.

A large amount of research has been dedicated to understanding the leaching behaviour of the TEs in terrestrial fuels and in their char and ash residues. In general, the extent of TE leaching from the char and ash residues cannot be correlated with the leachable fraction in the original feedstock [25]. The leachability of a TE depends on its chemical form (particularly oxidation state) [25–27] and on its spatial distribution in the fuel or residue [27]. Both of these properties can be altered during thermal conversion depending on the operating conditions. Formation of oxides, hydroxides and sulphates of the TEs are common under combustion conditions whereas reduced species tend to be formed under gasification conditions [11]. Certain TEs, especially those which volatilise and re-condense during thermal conversion (*e.g.* As, Sb, Se and Zn), can become enriched on char and ash particle surfaces [27] where they are more susceptible to leaching. The leachability of the TEs following thermal conversion is not only affected by the transformations of the TEs themselves but also by the transformations of the major and minor inorganic elements (*e.g.* Ca and S). The behaviour of the major and minor inorganic elements in the char and ash residues largely controls the pH of the leachate produced when the residue is brought into contact with water [28].

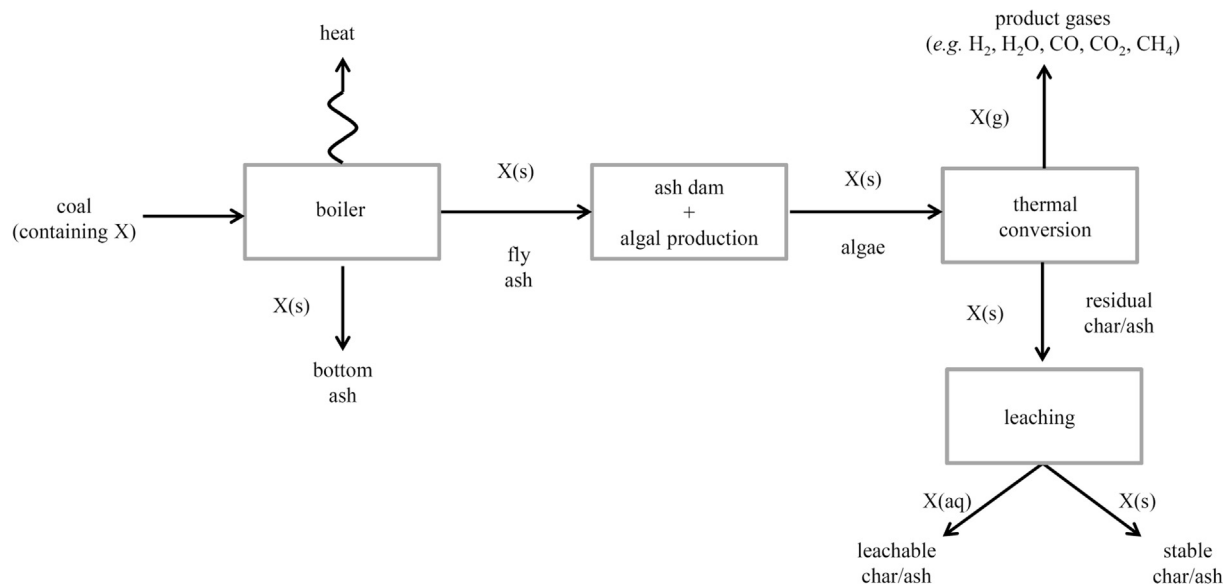


Fig. 1. Trace element flows and processes in the concept for combined algal bioremediation and thermal conversion. Trace element flows are indicated by the letter "X". The phase of the trace elements (*e.g.* solid, gas, aqueous) is indicated inside parentheses to the right of the letter "X".

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