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Abstract

Power generation from high-ash coals is a niche technology for power generation, but coal cleaning is deemed necessary to avoid problems associated with low combustion efficiencies and to minimize environmental burdens associated with emissions of pollutants originating from ash. Here, chemical beneficiation of coals using acid and alkali-acid leaching procedures is evaluated as a potential coal cleaning technology employing life cycle assessment (LCA). Taking into account the environmental benefits from firing cleaner coal in pulverized coal power plants and the environmental burden of the cleaning itself, it is demonstrated that for a wide range of cleaning procedures and types of coal, chemical cleaning generally performs worse than combustion of the raw coals and physical cleaning using dense medium separation. These findings apply for many relevant impact categories, including climate change. Chemical cleaning can be optimized with regard to electricity, heat and methanol use for the hydrothermal washing step, and could have environmental impact comparable to that of physical cleaning if the overall resource intensiveness of chemical cleaning is reduced by a factor 5 to 10, depending on the impact category. The largest potential of the technology is observed for high-ash lignites, with initial ash content above 30%, for which the environmental benefits from firing cleaner coal can outweigh the environmental burden of cleaning for some impact categories. We recommend for policy makers to use physical cleaning, as this clearly perform environmentally better, but encourage further research into the chemical cleaning process and optimization of the process as chemical cleaning may be necessary to comply
with current and emerging legislation on ash and sulphur content in coal where the removal efficiency from physical cleaning is insufficient.

Broader context

The use of fossil coal for generation of electricity is a major cause of many environmental problems globally. Pulverized coal-fired power plants currently account for 97% of total coal-based electricity generation globally, and are expected to constitute a significant proportion of the environmental burden attributable to power generation also in the future. Chemical cleaning of high-ash coals can potentially mitigate some environmental impacts from firing coal in pulverized power plants, as it allows reaching higher ash removal efficiencies as compared to physical cleaning, but virtually nothing is known about whether environmental benefits from firing cleaner coal outweigh environmental burdens of cleaning. Here, life cycle assessment (LCA) is employed to evaluate chemical beneficiation of coals using acid and alkali-acid leaching procedures. The results showed that demineralization is generally not a feasible option for mitigating environmental impacts, including impacts from climate change, except in few cases where regional and local impacts were improved for high-ash coal systems. This work highlights the current issues associated with chemical cleaning technologies and provides recommendations for stakeholders to resolve these.

1. Introduction

The use of fossil coal for generation of electricity is a major cause of environmental problems globally. Using life cycle impact assessment, Laurent and Espinosa\(^1\) showed that, while coal represented 41% of the global electricity produced in 2011, it contributed to more than 70% of the associated environmental burden for nearly all impacts on human health and ecosystems. This important contribution may decrease in the future, as the major focus of national policies is to decrease the share of coal in the power mix and to improve environmental performance of coal-based electricity generation\(^2,3\). The latter include shutting down small, inefficient power plants, imposing the deployment of cleaner coal technologies (CCTs) such as ultra-supercritical plants (e.g. in India, China, or South Africa), enforcing more stringent emission control and standards with respect to emissions of CO\(_2\), SO\(_2\), NO\(_x\), particulate matter (PM), or mercury (e.g. in European
Despite these initiatives, coal combustion in pulverized coal (PC) fired power plants, that currently accounts for 97% of total coal-based electricity generation (of which ca. 76% is old, subcritical power plants), can still be expected to take up a significant proportion of the total environmental burden attributable to power generation. Low-rank coals (with ash content above 30%) are relatively abundant as compared to high-rank coals and become increasingly important to secure a stable coal supply for power generation in pulverized power plants. Their extraction and firing becomes economically favorable as compared to import of high quality coals from elsewhere. Extraction and use of low-ranked coals thus takes place in Europe, U.S.A., China and India today, mainly due to depletion of high quality coal reserves and extraction of low rank coal being economically better than import of high quality coals. Power generation in some important coal using countries, including India, China, Czech Republic, Poland, South Africa, Romania and Turkey, currently relies strongly on these low-rank coals.

Coal cleaning to reduce ash content, usually below 30%, is deemed capable to avoid problems associated with low combustion efficiencies and minimize environmental burdens associated with emissions of airborne pollutants. This is true for both old (subcritical) and newer (e.g. supercritical or ultra-supercritical) combustion technologies. Coal cleaning is commercially done using physical methods, such as grinding of the raw coal followed by gravity-based processes (e.g. dense medium separation) and processes based on surface properties (e.g. froth flotation). These methods have relatively low ash removal efficiencies and are generally not suitable to coals where inherent ash-related minerals are finely disseminated in the coal matrix. In contrast, chemical cleaning using acid or alkali-acid leaching procedures are applicable to high-ash coals and allow removing ash more efficiently than physical methods. Because of this, chemical coal cleaning is seen as a complementary alternative to physical cleaning, allowing for achieving the required ash removal rates that cannot be achieved by solely using physical cleaning. Since the 1980s, a total of 26 studies have been published with focus on technological aspects of chemical cleaning using acid or alkali-acid leaching procedures (e.g. see Wijaya and Zhang and Meshram et al. for reviews). These studies show a great potential for chemical cleaning of coals, with ash removal efficiencies reaching up to ca. 97%, depending on the initial ash content and process conditions.

Chemical cleaning procedures are currently not widely employed at a commercial scale due to high costs associated with the requirements of chemicals and the need for dewatering of the post-
demineralization fine-sized slurry. To date, only one pilot plant has been constructed in Australia, which from 2010 to 2012 produced ultra clean coal (UCC, with ash content of ca. 0.1%) derived from a bituminous coal for application in integrated gasification combined cycle 19,20. In the future, chemical cleaning procedures can however become attractive also for PC firing combustion technologies, particularly for those coals for which physical beneficiation might not be a sufficient method for ash removal.

Coal cleaning can both improve and decrease the overall environmental performance of coal firing, depending on the type of environmental impact and stage of the coal combustion life cycle considered. Table 1 shows the implications of coal cleaning using chemical methods on environmental performance of power generation from cleaned coals. For example, reduced contents of sulfur and ash in the coal due to chemical leaching will allow reducing emissions of SO$_2$ and PM, thereby decreasing acidifying impacts on terrestrial ecosystems and damages to human health, and increased combustion efficiencies are expected to reduce climate change impacts up to 5 % 21 due to reduced emissions of CO$_2$ (per unit of electricity produced). By contrast, chemical leaching requires provision of heat and electricity, which can increase climate change impacts and toxicity-related impacts on human health and ecosystems due to the associated emissions of CO$_2$ and toxic substances. These potential tradeoffs between the environmental benefits of firing cleaner coal and the environmental burden of cleaning processes can be quantified using life cycle assessment (LCA). In LCA, resource consumption and emissions of pollutants stemming from the extraction of the raw materials, their manufacture and use or operations up to their end-of-life are inventoried and translated into impact indicator scores using substance-specific characterization factors for various life cycle impact categories. To date, LCA of power generation from coals cleaned chemically has not been reported in the literature.

The aim of this study is to evaluate chemical cleaning of coals using acid and alkali-acid leaching procedures as a potential coal cleaning technology. The focus is on chemical cleaning because of the lack of knowledge about its environmental performance in coal-based power generation; the goal is to provide a holistic environmental assessment of the technology to facilitate well-informed decisions on use of the technology. To illustrate the potential of the technology, all available variants of leaching procedures published so far for bituminous and sub-bituminous coals, and lignites, were compared (i) to each other, (ii) to physical cleaning using dense medium separation, and (iii) to conventional power generation from raw coals. The coals analysed in the
study vary with regard to the initial ash content (prior to leaching), and also include high-ash lignites with initial ash content above 30%.

Table 1. Changes introduced by switching from use of raw coal to coal cleaned chemically and their expected consequences for overall environmental performance.

<table>
<thead>
<tr>
<th>Differences induced by switching from raw coal to coal cleaned chemically</th>
<th>Expected consequences on environmental performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced airborne emissions from the power plant</td>
<td>Part of the ash and sulfur embedded in coal is emitted from the power plant as particulate matter (PM) in fly ashes, and as SOx. Lower ash and sulfur content will thus reduce PM and SOx emissions [27], which is expected to reduce acidification impact on terrestrial ecosystems and human health effects of particulate matter.</td>
</tr>
<tr>
<td>Coal content of hazardous metals like antimony, arsenic, cadmium, chromium, copper, cobalt, mercury, lead, manganese and nickel, generally present in trace amounts is reduced through the cleaning process [23]</td>
<td>The hazardous trace elements in the coal are emitted during the combustion or as part of the flue gas residue disposal. Removal of these pollutants will reduce toxic impact to humans and ecosystems. The environmental benefits of this removal cannot be included in this study because of missing data on the content of these elements in the uncleaned coal and their removal during coal cleaning.</td>
</tr>
<tr>
<td>Increased overall power plant efficiency</td>
<td>Ash influences the overall power plant efficiency mainly via decreased flame temperature, decreased heat absorption in heat exchangers, and increased deposits of ash as slag on the boiler heating surfaces. A decrease in the overall power plant efficiency is expected to increase impacts on climate change, as more carbon has to be fired per unit of electricity produced, which will increase overall CO2 emissions.</td>
</tr>
<tr>
<td>Increased life time of the plant</td>
<td>Reduction in ash content reduces fouling and corrosion of power plant components which increases the life time of the plant [24,25]. This is expected to decrease the need for steel and metals and thereby reduce impacts on resource (minerals) depletion.</td>
</tr>
<tr>
<td>Reduced amount of coal transported between the cleaning site (typically at mine) and the power plant</td>
<td>Chemical cleaning increases the higher heating value (HHV) of the coal, therefore less coal has to be transported from the cleaning site to the power plant per unit of electricity produced [26]. This will reduce fuel consumption for the transport and will thereby decrease the associated emissions of CO2 and PM. This is expected to lead to reduced fossil depletion and climate change impacts and respiratory effects on humans.</td>
</tr>
</tbody>
</table>

2. Methods

2.1. Life cycle assessment

The LCA was conducted in accordance with the requirements of the ISO standard [27] and the guidelines of the ILCD handbook [28]. The functional unit is defined as the “output to high voltage grid of 1 MJ of electricity produced from a pulverized coal power plant”. Power generation from chemically cleaned coals using various acid or alkali-acid leaching procedures was compared to power generation from coals cleaned physically using dense medium separation (gravity-based process), and to power generation from raw coals. Power generation from coal cleaned using dense
medium separation is the most widely used physical cleaning method of coal. Power generation from high-ash raw coal is rare, but is reported to take place in India\textsuperscript{13}.

Europe was chosen as the primary geographical scope of the assessment. However, as part of a sensitivity check, the comparisons were made using U.S.A. and China as alternative regions to test the validity of our conclusions and whether they change for other geographical regions. U.S.A and China were chosen as these are among the largest coal users worldwide\textsuperscript{29}. The system boundaries include the whole life cycle of the power generation, from the construction of the PC power plant and the extraction and supply of bituminous coal, sub-bituminous coal and lignite, through the cleaning process, to coal firing the plant, slag disposal, and decommissioning of the plant. In chemical cleaning, coal is first crushed using a hammer mill as crusher, and then leached in one step with an acid (acid leaching) or in two steps with first alkali and then acid (alkali-acid leaching) to dissolve and remove inert materials in the ash (see ESI † section S1 for details on chemical cleaning). In physical cleaning, coal is first crushed using a hammer mill and is next washed with water to remove inert impurities that are easily accessible and not embedded in the coal matrix \textsuperscript{30,31}. Raw coal is only crushed with a hammer mill before firing, but no washing procedure is applied.

The ILCD guidelines provide methodological guidance according to different decision situations, and the current study is in this context considered a micro-level decision support (type-A) situation. The use of chemical demineralization for cleaning of coal is not expected to have large structural changes on the market (e.g. installation of new coal firing capacity or opening new coal mines) compared to current coal practice, at least at the current state of maturity and operation of the chemical cleaning technology. Therefore, the comparison applies an attributional LCA approach, where average data and energy mixes are used. Bituminous and sub-bituminous coals are modelled to represent the European average situation where 78\% of the coal is extracted in Europe, and the rest is extracted in many parts of the World outside Europe. Lignite combusted in Europe is extracted in European countries only, primarily in Germany, Greece and Poland. Transport via shipping from extraction locations outside of Europe is included, as is storing and raw coal pretreatment, \textit{i.e.} washing). A European average electricity grid mix is used for the energy supply to the cleaning process and for the coal handling after it has been transported to Europe. Electricity and heat production are modelled as a European average. Alkali and acids that are produced in Europe are modelled for European conditions. Globally produced and traded commodities such as metals needed for construction are modelled as global production. The PC power plant and the subsequent slag treatment are modelled for European conditions. In cases of processes with
recovery of commodities, system expansion was performed, assuming that recovered chemicals
(acid and alkali) substitute the production of virgin chemicals, and that ash extracted from coal
during chemical cleaning, being a lime product, substitutes virgin lime and gypsum as input for
cement production. For U.S.A. and China, different processes were used for coal extraction,
electricity generation, and PC power plant technology (see Table S1 in ESI † for more information
on the geographical scope).

The product systems were modeled in the LCA software GaBi, version 4.3 (PE International,
Germany). Environmental impact scores were calculated using the ReCiPe (version 1.05)
characterization factors, as implemented in GaBi.
Fig. 1. System boundaries for power generation from raw coal (upper), for coal cleaned using physical cleaning (middle) and for coal cleaned using chemical cleaning with acid or alkali-acid leaching (lower).
2.2. Data collection and model parameters

Data on types of equipment for chemical cleaning are based on the full-scale process patented by Brooks et al.\textsuperscript{33}, and are combined with data on leaching process conditions, including types and concentration of acids and/or alkali, reaction temperature and duration. This data was retrieved from published studies, available up to September 2014, identified using ISI Web of Knowledge (version 5.7; Thomson Reuters, New York, NY), and were included if the following criteria were met: (i) types of alkali and/or acid are reported, (ii) alkali and/or acid concentrations, cleaning process temperatures and cleaning duration are reported, (iii) initial ash, sulfur, nitrogen, carbon and oxygen contents in the coal are reported, and (iv) final ash contents of the coal are reported. Cited and citing studies that were found to contain relevant data were then consulted to complement the search, and this process was iterated until no new study was found. Studies on cleaning with organic solvent extraction and those with irradiation (such as microwave or ultrasonic) as leaching pretreatment, were excluded. In total, 10 studies (14–18,34–38) were found which met the data requirement criteria. They contain 132 data points for alkali-acid leaching and 107 data points for acid leaching, with 151, 36 and 52 measured data points for bituminous, sub-bituminous and lignite coals, respectively (see section S3 in ESI † for details of the data). Calculated higher heating values (HHV) ranged from 14.9 to 29.5 MJ/kg, depending on the type of coal and the final ash content (Fig. 2). Ash removal efficiencies ranged from 0.05 to 0.97 across all coals, and were the highest for chemical cleaning of high-ash lignites (data not shown).

Model parameters for the processes included within the system boundaries are synthesized in Table 2 and references given. Data for the PC power plant are based on the inventory for a subcritical PC power plant as included in ecoinvent v2.2\textsuperscript{39} and were modified to reflect the differences between different types of coal with regard to combustion efficiency and emission of pollutants. During combustion, all C, S and N compounds were assumed to be oxidized to CO\textsubscript{2}, SO\textsubscript{x}, and NO\textsubscript{x}. Emissions of these gases depend on the installed flue gas cleaning systems, which vary between plants (see Table 2).
Fig. 2. Final ash content and HHV values of raw and cleaned coals. Error bars indicate the 95% variability intervals. The HHV was calculated using the formula

\[
HHV = 0.341 \times C + 1.323 \times H + 0.0685 \times Ash - 0.1194 \times (O + N)
\]

which is based on 700 coal samples, where \(C, H, O, N\) and \(Ash\) are fractions of the respective element and ash contents in the coal (in kg\_element/kg\_coal and kg\_ash/kg\_coal, respectively)\(^{40}\).
Table 2. Model parameters and data sources.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average (min - max)</th>
<th>Unit</th>
<th>Note</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal power plant</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power plant efficiency at standard ash content (E₀)</td>
<td>0.366 (0.260 – 0.430)</td>
<td>MJ/MJ</td>
<td>The power plant efficiency at standard (6% ash content (E₀). Assumed equal to energy efficiency across subcritical, supercritical and ultra-supercritical power plants in EU member states (see Table S3 in ESI †). The average and variability ranges for Europe were also applied for power plants in China and U.S.A. This choice does not influence the main goal of this study i.e. the comparison between coal cleaning technologies, but will to some extent influence the environmental performance of coal burning in general.</td>
<td></td>
</tr>
<tr>
<td>Overall power plant efficiency (E)</td>
<td>0.362 (0.245 – 0.432)</td>
<td>MJ/MJ</td>
<td>The overall efficiency of the power plant (E) in MJ electricity produced per MJ of thermal input. Calculated as a product of the plant-specific efficiency at standard ash content (E₀) and the coal-specific, ash-dependent efficiency ratio (ER) using the formula ( E = E₀ \cdot ER ) (2)</td>
<td>calculated</td>
</tr>
<tr>
<td>Efficiency ratio (ER)</td>
<td>0.988 (0.941-1.005)</td>
<td>(-)</td>
<td>The efficiency ratio takes into account effects of ash content (Ash, in fraction) on the boiler efficiency, auxiliary efficiencies, steam efficiency, turbine efficiency and generator efficiency. It increases with decreasing ash content. Calculated using the formula ( ER = 1.005 - 0.05189 \times Ash - 0.52841 \times Ash^2 ) (25)</td>
<td>calculated</td>
</tr>
<tr>
<td>Flue gas cleaning, NOx removal efficiency</td>
<td>80 (75 - 85)</td>
<td>%</td>
<td>Range of values measured for NOx removal using selective catalytic reduction (SCR) process, being one of the most common post-treatment methods.</td>
<td></td>
</tr>
<tr>
<td>Flue gas cleaning, SOx removal efficiency</td>
<td>89 (80 - 98)</td>
<td>%</td>
<td>Range of values measured for SOx removal using flue gas desulfurization (FGD), that utilizes a variety of slurry or sorbent materials to scrub gases</td>
<td></td>
</tr>
<tr>
<td>Flue gas cleaning, PM removal efficiency</td>
<td>97 (95 – 99)</td>
<td>%</td>
<td>Range of values for coal power plants, where on average 3% of initial ash content is emitted to air as particulate matter and the remaining is captured and collected as bottom ash and landfilled.</td>
<td>ecoinvent v2.2 [5]</td>
</tr>
<tr>
<td>Chemical cleaning using acid or alkali-acid leaching procedures</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centrifuge, electricity use</td>
<td>1.5 (0.03 – 3.21)</td>
<td>MJ/m³ liquid</td>
<td>The electricity required for removing liquid from the coal slurry. Values measured for high- and low-gravity centrifuges of sizes 74 x 208 and 90 x 225 (cm diameter x 208 cm length), respectively. Assumed equal in energy used for coal slurry.</td>
<td>assumed</td>
</tr>
<tr>
<td>Filter press, electricity use</td>
<td>0.88 (0.66 – 1.10)</td>
<td>MJ/m³ liquid</td>
<td>The electricity required for removing liquid from the coal slurry. Measured for algae recovery and assumed similar in energy used for coal slurry.</td>
<td>assumed</td>
</tr>
<tr>
<td>Solid content in slurry after filter press</td>
<td>42.5 (35 – 50)</td>
<td>%</td>
<td>The solid content present in the coal slurry after filter press, measured for batch filter presses used for dewatering wastewater with high solids content and assumed similar in energy used for coal slurry.</td>
<td>assumed</td>
</tr>
<tr>
<td>Hydrothermal washing heat use</td>
<td>3573</td>
<td>MJ/m³ slurry</td>
<td>The energy for heat and electricity used for running the hydrothermal washing process, calculated from heat equation for a mixture of water, methanol and coal to heated up to 240 °C, as explained in the ESI † section S5</td>
<td>calculated</td>
</tr>
<tr>
<td>Water to methanol ratio for hydrothermal washing</td>
<td>1:1</td>
<td>kg/kg</td>
<td>The ratio in which methanol and water are mixed for the hydrothermal washing. A solvent such as methanol is stated as a requirement by Brooks et al. and is applied in the base scenario. However, the literature providing the data points used is not reporting whether a solvent is used during washing of the coal, and in many cases only water is applied. We therefore perform a sensitivity test using different ratios of methanol to water.</td>
<td></td>
</tr>
<tr>
<td>Liquid (water + methanol) to coal ratio for hydrothermal washing</td>
<td>4:1</td>
<td>kg/kg</td>
<td>The default mixing ratio of water and methanol liquid with coal for the hydrothermal washing as used in the base scenario</td>
<td></td>
</tr>
<tr>
<td>Coal drying, heat use</td>
<td>8.1</td>
<td>MJ/kg water</td>
<td>The ambient temperature of the coal. Assumed equal in energy used for heating and removing water via drying to obtain clean water-free coal.</td>
<td></td>
</tr>
<tr>
<td>Ambient liquid temperature</td>
<td>12</td>
<td>°C</td>
<td>The ambient temperature of the liquid used for coal leaching. This affects the energy requirements for heating the water during demineralization.</td>
<td>assumed</td>
</tr>
<tr>
<td>Reagents recovery efficiency</td>
<td>85</td>
<td>%</td>
<td>Alkali and the acids are recovered after the leaching process using lime and gypsum, respectively. The efficiency of the recovery process for recovery of alkali and acid is based on one source only, hence no range is provided. The recovery reactions are as follows:</td>
<td></td>
</tr>
<tr>
<td>Reagents recovery electricity use</td>
<td>0.005</td>
<td>MJ/kg</td>
<td>The electricity use for recovery of alkali and acids</td>
<td></td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-------</td>
<td>-------</td>
<td>-----------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Acid or alkali concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>11.6</td>
<td>(5.0 – 30.0)</td>
<td>%</td>
<td>Aqueous concentration of HCl in the acid leaching step</td>
</tr>
<tr>
<td>HNO₃</td>
<td>19.0</td>
<td>(5.0 – 30.0)</td>
<td>%</td>
<td>Aqueous concentration of HNO₃ in the acid leaching step</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>15.5</td>
<td>(5.0 – 30.0)</td>
<td>%</td>
<td>Aqueous concentration of H₂SO₄ in the acid leaching step</td>
</tr>
<tr>
<td>HF</td>
<td>9.5</td>
<td>(1.3 - 25.5)</td>
<td>%</td>
<td>Aqueous concentration of HF in the acid leaching step</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>12.5</td>
<td>(2.5 – 30.0)</td>
<td>%</td>
<td>Aqueous concentration of H₂O₂ in the acid leaching step</td>
</tr>
<tr>
<td>NaOH</td>
<td>28.5</td>
<td>(2.0 – 98.0)</td>
<td>%</td>
<td>Aqueous concentration of NaOH in the alkali leaching step</td>
</tr>
<tr>
<td>Temperature of the acid leaching step</td>
<td>84.5</td>
<td>(25.0 – 100.0)</td>
<td>°C</td>
<td>The temperature during the acid leaching</td>
</tr>
<tr>
<td>Duration of acid leaching step</td>
<td>2.4</td>
<td>(0.2 – 8.0)</td>
<td>hours</td>
<td>The duration of the acid leaching</td>
</tr>
<tr>
<td>Temperature of alkali leaching step</td>
<td>146.4</td>
<td>(85.0 – 210.0)</td>
<td>°C</td>
<td>The temperature during the alkali leaching step</td>
</tr>
<tr>
<td>Duration of alkali leaching step</td>
<td>1.7</td>
<td>(0.5 – 24.0)</td>
<td>hours</td>
<td>The duration of the alkali leaching step</td>
</tr>
<tr>
<td>Sulfur reduction efficiency due to chemical cleaning</td>
<td>20 (9 – 48)</td>
<td>%</td>
<td>Reduction of sulfur content in the coal as a function of alkali-acid leaching predicted from NaOH concentration, acid concentration, time of alkali leaching and time of acid model using a model developed based on literature data (see ESI † section S6). The model has been validated against external data, and its predictive power corresponds to a predictive squared correlation coefficient for external validation (Q²) equal to 0.8.</td>
<td>calculated</td>
</tr>
<tr>
<td>Nitrogen reduction efficiency due to chemical cleaning</td>
<td>0</td>
<td>%</td>
<td>No nitrogen reduction considered, as literature on nitrogen content from chemical demineralization is inconclusive. A number of sources state that nitrogen content increases with alkali-acid leaching 59,49,50. This has only been shown where nitric acid is used, in these cases the nitrogen containing acid may react to form nitrogen-bearing species within the coal59.</td>
<td>assumed</td>
</tr>
</tbody>
</table>

### Physical cleaning using dense medium separation (gravity-based method)

| Ash removal efficiency | 50 (16 – 68) | % | The ash removal efficiency from the coal after physical cleaning using dense medium separation measured for various dense medium separation procedures. | 51 |
| Sulfur removal efficiency | 48 (10 – 84) | % | The sulfur removal efficiency from the coal after physical cleaning measured for various dense medium separation procedures. | 51 |
| Electricity use | 0.027 (0.022 – 0.032) | MJ/kg coal treated | The electricity use for physical cleaning of coal at mine measured for a dense medium separation procedures process. | 52 |

### Transportation

| From coal storage to power plant | 100 | km | By lorry | assumed |
| From coal storage to demineralization plant | 10 | km | By lorry | assumed |
| From demineralization plant to power plant | 100 | km | By lorry | assumed |
2.3. Sensitivity analysis

Sensitivity of impact scores to uncertain or variable model parameters was done by calculating normalized sensitivity coefficients ($S_{coef}$), according to Eq. 1 $^{53,54}$:

$$S_{coef} = \frac{\Delta IS}{IS_0} / \frac{\Delta a_k}{a_{k,0}}$$

where $a_{k,0}$ is the input parameter value, $IS_0$ is the impact score calculated for the $a_{k,0}$, $\Delta a_k$ is the difference between the default input parameter and the perturbed input parameter, $\Delta IS$ is the difference between $IS_0$ and the impact score calculated for the perturbed parameter value. All input parameters were perturbed by 25%. All parameters in Table 2 were included in the sensitivity analysis. Among all 239 chemical cleaning combinations, the $S_{coef}$ was calculated for a total of 16 combinations, selected to represent a range of chemical cleaning process conditions, (i.e. the highest and the lowest values of: NaOH concentration, acid concentration, time of the alkali leaching step, temperature of the alkali leaching step, time of the acid leaching step, and temperature of the acid leaching step), a range of initial ash contents (i.e. the highest and lowest initial ash content) and a range of ash removal efficiencies (i.e. the highest and the lowest ash removal efficiency). A parameter is considered important if average $|S_{coef}| \geq 0.3$, or if the largest $|S_{coef}| \geq 0.5$, corresponding to a medium and large sensitivity, respectively $^{55}$.

2.4. Uncertainty and variability analysis

Parameter uncertainties stem from the lack of knowledge about the actual value of a parameter $^{56}$, e.g. electricity use of a centrifuge. By contrast, variability is the inherent variance that will exist between similar processes depending on technological level and spatial location, e.g. power plant efficiency at standard ash content $^{56}$. Here, parameter uncertainty was assessed together with variability by means of a Monte Carlo analysis, using parameters which were found important in the sensitivity analysis (Table 3). They were assigned standard deviations based on the min-max ranges in Table 2, accounting for their uncertainty and variability. Normal distributions were assumed. Differences in impact scores between the compared systems were considered significant if the calculated 95% probability ranges of the impact scores from 1000 iterations did not overlap $^{57}$.
Table 3. Uncertain or variable parameters included in the Monte Carlo simulation and the associated relative standard deviation.

<table>
<thead>
<tr>
<th>Uncertain or variable parameter</th>
<th>Average (relative standard deviation)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency of NOx removal</td>
<td>0.8 (6%)</td>
<td>Based on literature 22</td>
</tr>
<tr>
<td>Efficiency of SOx removal</td>
<td>0.89 (10%)</td>
<td>Based on literature 22</td>
</tr>
<tr>
<td>Power plant efficiency</td>
<td>0.366 (12%)</td>
<td>Mean and standard deviation are based on power plant overall efficiencies of European countries 40</td>
</tr>
<tr>
<td>Centrifuge electricity use</td>
<td>1.5 (30%)</td>
<td>Based on literature 24</td>
</tr>
<tr>
<td>Filter press electricity use</td>
<td>0.88 (25%)</td>
<td>Based on 42, because variability ranges were not available, a relative standard deviation of 25% is assumed to account for large variations</td>
</tr>
<tr>
<td>Sodium hydroxide recovery efficiency</td>
<td>0.85 (25%)</td>
<td>Based on 46, because variability ranges were not available, a relative standard deviation of 25% is assumed to account for large variations, varying between a recovery efficiency of 64 – 100 %</td>
</tr>
<tr>
<td>Acid recovery efficiency</td>
<td>0.85 (25%)</td>
<td>Based on 46, because variability ranges were not available, a relative standard deviation of 25% is assumed to account for large variations, varying between a recovery efficiency of 64 – 100 %</td>
</tr>
<tr>
<td>Physical ash removal efficiency</td>
<td>0.50 (33%)</td>
<td>The fraction of ash left in coal after mechanical treatment at mine, using crushing and gravity separation 51</td>
</tr>
<tr>
<td>Mechanical sulfur removal efficiency</td>
<td>0.52 (26%)</td>
<td>The fraction of sulfur left in coal after mechanical treatment at mine, using crushing and gravity separation 51</td>
</tr>
</tbody>
</table>

3. Results and discussion

Below, we present results for four selected impact categories, which represent typical impact profiles observed for all 18 impact categories (results for all impact categories are presented in Fig. S2 in ESI †). Next, the potential of the chemical cleaning technology as a coal beneficiation method, and the broader applicability of our findings, are discussed.

3.1. Does coal cleaning bring environmental benefits?

Fig. 3 shows that, irrespective of the initial ash content, coals cleaned chemically perform significantly worse in an overall life cycle perspective than raw coals and coals cleaned physically for the impact category climate change. For acidification impacts on terrestrial ecosystems and impacts from PM on human health, impact scores overlap, whereas for freshwater ecotoxicity (toxic impacts on freshwater ecosystems), the environmental performance of the chemically cleaned coal depends on the initial ash content of the coal: for low-ash coals chemical cleaning performs worse as compared to raw coal, and the opposite is observed for high-ash coals. Further, freshwater ecotoxicity impact scores for coals cleaned chemically peak at 30% of initial ash content.
The increase in impact scores with initial ash content up to 30% for freshwater ecotoxicity (but also for freshwater eutrophication, PM formation and other toxicity-related impact categories, see Fig. S2 in ESI †) is primarily caused by emissions of particles and leaching of heavy metals and phosphate from landfilling of residual (bottom) ash. These emissions are naturally higher for high-ash coals. Thus, there is some potential for avoiding environmental problems caused by firing coals if the ash is separated from the coal before the firing. Indeed, the decrease in impact scores for chemically cleaned high-ash coals (containing > 30% ash in raw coal) is due to a very efficient cleaning of lignites, for which up to 90% ash removal efficiency can be reached using acid or alkali-acid leaching procedures17. In contrast, the ash removal efficiency for physical cleaning generally does not depend on the coal type, which explains why environmental performance of high-ash lignites cleaned chemically improves relative to these coals cleaned physically.

**Fig. 3.** Impact scores and the associated 95% confidence intervals per functional unit (“output to high voltage grid of 1 MJ of electricity produced from a pulverized coal power plant”) as a function of initial ash content.
of ash content in the raw coal, shown for each of the four selected impact categories. The results are shown for the European scenario.

**Fig. 4.** Contribution of life cycle processes to total impact scores for coal firing using chemical cleaning (alkali-acid leaching) of coals with different initial ash contents. The results are shown for the European scenario.
3.2. Can chemical cleaning become an environmentally sound approach for coal beneficiation?

Despite the potential benefits of chemical cleaning of high-ash coals for some impact categories, our results show that burden shifting might occur if only environmental problems directly caused by ash are considered. Indeed, impact scores for other relevant impact categories including climate change and depletion of resources (land, water, minerals and fossils) are increased when ash is removed before firing (see Fig. 3 and Fig. S2 in ESI †). Such trends are caused by non-ash-related emissions, which have large contributions in other environmental impacts and stem from the cleaning process. For example, while the reduction in PM emissions from the firing of the chemically-cleaned lignites outweigh the increase in PM emissions from the cleaning processes, thus resulting in an overall decrease of impact scores for the PM formation impact category, the opposite trend is observed for climate change and other impact categories (see Fig. 3). Improvements in the environmental performance of chemical cleaning should therefore focus on optimization of cleaning procedures in order to minimize all relevant environmental impacts.

To identify improvement potentials for the chemical cleaning technology a process contribution analysis was conducted, i.e. identifying the processes with the largest environmental burden. Fig. 4 shows that the largest contributors to environmental impacts are (i) the electricity consumption for centrifugation in the alkali step of the leaching procedure, and (ii) the production of methanol for the hydrothermal washing step of the cleaning procedure. The contributions of these two processes were above 50% of the total impact score for many impact categories. The sensitivity analysis further confirmed that these processes had the largest influence on impact scores (see Table S6 in ESI †). Hence, there is a potential for improving the environmental performance of the chemical cleaning technology if the electricity demand for chemical demineralization and the methanol use for the hydrothermal washing step are optimized.

In our study of chemical cleaning we had to rely on data from the pilot scale process combined with parameters retrieved from laboratory measurements and estimations based on physical relationships (e.g. energy required for heating a liquid solution). However, commercial scale processes are often seen to have smaller environmental impacts due to the use of more efficient use of processes and feedstock58 compared to laboratory scale where efficiency is less important and focus is on developing the cleaning process and achieving useful results. Thus, it cannot be ruled out that the overall demand for chemicals and energy will be smaller when chemical cleaning is performed at commercial scale. Because chemical cleaning is still a relatively new and immature
technology some improvement with regard to use of energy and feedstock as a result of upscaling can be expected. Yet, our analysis shows that a reduction in total electricity and heat use in chemical cleaning by a factor of 5 to 10, depending on the impact category would make chemical cleaning perform comparably to physical cleaning; this is illustrated in Fig. 5-1 for the climate change impact category. Achieving such reduction poses a strong challenge for the technology and seems unlikely. For petrochemical production processes, which share some similarities with chemical cleaning (e.g. centrifuge, filtering and heating), the energy consumption can be reduced by 16 % - 20 % by adopting best available technologies (BAT) \(^{59,60}\). The heat demand from upstream sources can be reduced by utilizing low grade waste heat (energy pinching), which is estimated to increase energy efficiency by circa a factor 1.2 \(^{61-64}\), while electricity efficiency may be increased by use of kinetic energy recovery systems or improving the efficiency of electricity using systems, this can yield electricity savings between 5 % - 40 % \(^{64,65}\).

Methanol is produced from natural gas, through synthesis gas, which is then converted to methanol using metal oxide catalysts \(^{39,66}\). Because methanol is a key intermediary product and is vital for the production of many globally-used commodities (e.g. formaldehyde and solvents), finding cleaner alternatives for methanol appears unlikely. However, the use of a solvent such as methanol during the hydrothermal washing step is not absolutely necessary; Mukherjee \(^{67}\) already showed that alkali-acid cleaning combined with washing in a methanol solution did not show improved cleaning efficiencies compared to similar alkali-acid leaching studies where the same coal was washed with pure water \(^{18,34,38}\). We therefore tested if excluding methanol from the cleaning procedure improves environmental performance of chemical cleaning. Figure 5-2 shows that although methanol contributes substantially to a number of impact categories, the influence of excluding it from the hydrothermal washing step on impact scores is modest. This is because chemical cleaning generally perform worse than physical cleaning for the impact categories where methanol is found to be an important contributor, and whether methanol is included makes little difference on the comparison (see ESI Fig. S2). Thus, while phasing out methanol and replacing it with water is overall an important improvement of the cleaning procedure, it is not sufficient for chemical cleaning to perform better as compared to physical cleaning.

Developers of leaching procedures typically focus on optimizing reaction conditions and selection of appropriate acids, which in this study are seen to have relatively small contribution to total environmental impacts and are not seen to influence impact scores significantly (\(S_{\text{coef}}\) typically below 0.1, see Section S9 in ESI †). Thus, from the environmental performance perspective, higher
concentrations of acids and alkali and higher leaching temperatures and durations can be justified if they allow for increasing ash removal efficiencies and thereby increasing the environmental benefits associated with firing cleaner coal. This is observed for lignites, of which many have their initial ash content equal to 35%: more severe cleaning conditions with regard to temperatures and concentrations of chemicals do not translate into higher environmental impacts.

In summary, chemical cleaning is not likely to become an environmentally sound approach for coal beneficiation, unless developers of chemical cleaning procedures (i) use water instead of methanol in the washing step, (ii) focus on achieving very high ash removal efficiencies by optimizing the use of alkali and acids, and (iii) find more attractive, environmentally speaking, ways of separating liquid from coal slurry after each washing steps.

3.3. Applicability of the findings for other geographic locations

Our conclusions about the overall poor performance of chemical cleaning are not expected to change when assuming coal power production in U.S.A. or China. Even though impact scores for these two countries are higher for many impact categories as compared to Europe, chemical cleaning is generally seen as the worst alternative in terms of environmental impacts. However, for terrestrial acidification impacts (see Fig. 5), PM formation and marine eutrophication in the Chinese scenario, impact scores for chemical cleaning are lower than those for the raw coal (data not shown). Chinese plants in our model have lower SO₂ cleaning efficiencies and PM removal efficiencies. Hence chemical cleaning becomes environmentally beneficial as it allows removing a part of sulfur and ash from the coal that otherwise would have been emitted as SO₂ and PM. This could suggest that chemical cleaning could be an environmentally sound technology for ash removal in regions where pollutant emission regulations are not as stringent as in Europe. However environmental burden shifting might still occur as for other impact categories, just as for climate change, chemical cleaning performs worse than physical cleaning or firing of raw coal.

The overall power plant efficiency was by far the most influential parameter (with $S_{coer}$ equal to -0.8 for all impact categories), hence, an increase in the overall power plant efficiency will reduce environmental burdens associated with power generation. However, simply shifting to a power plant with a higher overall efficiency will not make chemical cleaning an environmentally sound coal beneficiation options, unless large reductions in combustion efficiencies due to high ash contents are observed for highly-efficient plants. Such situations, however, do not apply to PC power plants. Yet, a reduction of ash content below 0.1% allows coal firing in an integrated
gasification combined cycle. Such application supports our findings that chemical cleaning technology may be environmentally beneficial when used to clean high ash coals with very high removal efficiencies (see Section 3.2).

**Fig. 5.** Impact scores for climate change in the European scenario are shown for a) the base scenario, b) for the scenario where the electricity and heat use for chemical cleaning was reduced by a factor 5 and c) for the scenario where the electricity and heat use was reduced by a factor 10. Underneath, impact scores for freshwater ecotoxicity in the European scenario are shown in d) for the base scenario using 1:1 water to methanol ratio, in e) using 3:1 water to methanol ratio and in f) where methanol is excluded and only water is used during the hydrothermal wash. Finally, impact scores for terrestrial acidification are shown for three different geographical scopes g) the base scenario *i.e.* Europe, h) U.S.A. and i) China.
4. Conclusions and recommendations for policy makers

The increased use of low rank coals for power generation has resulted in the implementation of stricter legislation on ash and sulphur contents in the coal, primarily to reduce air pollution and transport costs. For instance, as part of the “Interim Measures on the Management of Commercial Coal Quality“, China has imposed restrictions on ash and sulphur contents in lignites for commercial use which must stay below 30% and 1.5% respectively to reduce emissions from coal burning\textsuperscript{68}. India has banned coal with ash content above 34 % in order to reduce impacts and costs from the often long transports inside the country\textsuperscript{10}. Increased research and development of chemical coal cleaning has been recommended in a report to the U.S. Secretary of Energy by the National Coal Council, NCC\textsuperscript{69}(which serves as an advisory council to the Secretary of Energy and NCC members comes from both industry and academia). This new legislation is expected to increase demand for chemical cleaning technologies in the future, particularly for high-ash coals with ash and sulphur being strongly embedded in the coal matrix, for which physical cleaning is not sufficient method for cleaning. Yet, as we showed that chemical cleaning of coals for firing in PC power plants in general is not an environmentally sound option for coal beneficiation, we recommend policy makers that coal cleaning using acid or alkali-acid leaching procedures should not be considered for direct implementation as a coal beneficiation technology. We note, however, that chemical cleaning is a relatively immature technology and, as showed, its environmental performance of chemical cleaning is expected to improve when upscaling from the laboratory scale to the commercial scale is done. These improvements can be achieved by phasing out methanol in the washing step, increasing higher ash removal efficiencies by optimizing the use of alkali and acids, and finding more attractive, environmentally speaking, ways of separating liquid from coal slurry after each washing step. When these measures are undertaken, chemical cleaning might become environmentally attractive technology that can complement physical cleaning methods for ash removal for high-ash, difficult to treat coals. We stress that life cycle based approaches, such as LCA must be used to determine for which coals and cleaning procedures, chemical cleaning can be considered as potential beneficiation technology to avoid environmental burden shifting which occurs when environmental benefits of firing cleaned coal do not outweigh environmental burden of the cleaning. Finally, for high-ash coals where ash is relatively easy to remove and for coals with low ash content, we recommend policy makers to focus on physical methods of cleaning. They clearly perform better in a life cycle perspective as compared to chemical cleaning or combustion of
raw coal and it is not likely that they will be able to compete with physical cleaning in terms of environmental performance even when eco-design measures are undertaken.

5. Notes and References

† Electronic Supplementary Information (ESI) available: Supplementary Methods (Figure S1; Tables S1-S4) and Supplementary Results and Discussions (Figure S2; Tables S5-S7).


NCC, Reliable & Resilient The Value of Our Existing Coal Fleet An Assessment of Measures to Improve The Value of Our Existing Coal Fleet Reliable & Resilient, The National Coal Council, 2014.