Effect of uncertainty in sorbent characteristic on techno-economic feasibility of carbonate looping for decarbonisation of coal-fired power plant

Dawid P. Hanak

Energy and Power Theme, School of Water, Energy and Environment, Cranfield University, Bedford, Bedfordshire, UK

Correspondence
Dawid P. Hanak, Energy and Power Theme, School of Water, Energy and Environment, Cranfield University, Bedford, Bedfordshire MK43 0AL, UK. Email: d.p.hanak@cranfield.ac.uk

Summary
Carbon capture, utilisation and storage (CCUS) technologies are forecasted to significantly contribute to the decarbonisation of the power sector. Chemical solvent scrubbing is now considered the most mature CCUS technology. Yet, its integration with fossil fuel power plants is forecasted to reduce the net efficiency of the entire process by at least 7% points, resulting in the avoided CO2 cost of 35 to 75 €/tCO2. Carbonate looping (CaL) has been demonstrated to be an emerging technology for decarbonisation of the power sector with lower efficiency (>5% points) and economic penalties (10-30 €/tCO2). The key challenge that may influence the viability of CaL is the decay in the sorbent CO2 uptake. Such a deterioration in sorbent performance is usually accounted for in the techno-economic assessments via semi-empirical correlations. Yet, such correlations include fitting parameters based on experimental data that is, in turn, associated with ±20% measurement error. This study employed a stochastic approach to quantify the impact of such uncertainty in the sorbent characteristics on the techno-economic performance of a 580 MWel coal-fired power plant with CaL retrofit. The stochastic assessment showed that the most likely figures for the efficiency penalty would fall between 7.7 and 8.7% points, with a median of 8.08% points. Such a figure was higher than the one determined using the deterministic approach (7.85% points). Moreover, the estimated CO2 avoided cost was between 29.74 and 46.50 €/tCO2, with a median of 35.94 €/tCO2. Such a figure was higher than that obtained in the deterministic assessment (32.40 €/tCO2). It implied that the economic assessment using the deterministic approach could underestimate the costs associated with the CaL retrofits. This study, therefore, revealed that the uncertainty in the sorbent characteristics would influence the techno-economic viability of the CaL retrofits.

Novelty statement
This study demonstrated that the uncertainty in the sorbent characteristics would influence the techno-economic viability of the CaL retrofits. It showed...
that the cost of CO₂ avoided fell between 29.74 and 46.50 €/tCO₂, with a median of 35.94 €/tCO₂. Such a figure was higher than that obtained in the deterministic assessment (32.40 €/tCO₂). The outcome of this study implies that the economic assessment using the deterministic approach could under-estimate the costs associated with the CaL retrofits.

**KEYWORDS**
calcium looping, carbon capture, decarbonisation, stochastic modelling, techno-economic analysis

1 | INTRODUCTION

The recent report by the IPCC stated with high confidence that climate change induced by anthropogenic activities has already exhibited widespread impacts and damages to people and ecosystems. It includes heat-related mortality, warm-water collar bleaching and mortality, and drought-related tree mortality. The increased frequency and intensity of extreme weather events already have negatively impacted the water and food supply chains. According to the IEA, the combustion of fossil fuels in the power sector is responsible for 50% of the global energy-related CO₂ emissions. Therefore, full decarbonisation of the power sectors is critical to limiting the mean temperature increase below 1.5°C, in line with the Paris Agreement. Carbon capture, utilisation and storage (CCUS) technologies are forecasted to significantly contribute to the decarbonisation of the power sector. These are expected to correspond to approximately 15% of the cumulative global CO₂ emission reductions between 2020 and 2070, contributing to the decarbonisation of power systems reliant on fossil fuels and bioenergy. It is worth pointing out that the latter will result in negative CO₂ emissions, providing reliable offsets for other difficult-to-abate industries. Yet, the viability and environmental benefits of bioenergy with CCUS need to account for the full biomass supply chain.

Among three main approaches applicable to CCUS for the power industry, post-combustion CCUS technologies are currently considered the most viable approach for reducing CO₂ emissions from the combustion of fossil fuels. It is primarily because a limited number of modifications is necessary to integrate these technologies into the state-of-the-art designs of the conventional power plants. Integration of the post-combustion CO₂ capture technologies will also have a limited impact on the power plant flexibility, which will be an increasingly important characteristic of the fossil fuel power plants at higher penetration levels of intermittent renewables in the future energy systems. Chemical solvent scrubbing is now considered the most mature technology for deploying CCUS in the power sector. It has already been demonstrated commercially at Petra Nova and Boundary Dam coal-fired power plants (CFPP). Capocelli and De Flaco revealed that the efficiency penalty for post-combustion CO₂ capture using monoethanolamine can fall between 10.0% and 13.5% points. Despite the fact that the significant advancements in technology development and consideration of alternative chemical solvents to conventional monoethanolamine, such as diethanolamine, 2-amino-2-methyl-1-propanol, or methyldiethanolamine, integration of chemical solvent scrubbing to the fossil fuel power plants is still forecasted to result in the minimum net efficiency penalty of 7.7% points. For this reason, alternative post-combustion CO₂ technologies are being considered.

Carbonate looping (CaL), which considers natural sorbents such as limestone, has been proven to be a viable process for reducing CO₂ emissions from power generation and hydrogen production technologies. Shimizu et al. demonstrated that the CFPP retrofitted with CaL resulted in 1.4% points lower efficiency penalty than oxy-fuel combustion. Romeo et al. demonstrated that the CaL retrofit to a 450 MWel CFPP would reduce the net efficiency of the host plant by 7.9% points. However, their study revealed that the net power output of the host plant retrofitted with CaL would increase by more than 45%. The current literature presents many alternative layouts and sorbents for CaL that present the opportunity to achieve efficiency penalties lower than 5% points. Pillai et al. showed that integrating CaL into biomass-fired power plant would reduce its net efficiency by 1.94% points (without compression). Their study also assessed a double CaL layout, where the heat for calcination was supplied by hot CaO heated in the external biomass boiler. Such a layout resulted in a net efficiency penalty of 0.1% points (without CO₂ compression) and 4% points (with CO₂ compression). Moreover, Pillai et al. demonstrated that the CaL retrofit to a natural gas combined cycle plant and dimethyl ether production would result in an efficiency penalty of 8.2% points and a CO₂ avoided cost of 15 €/tCO₂. As a result of superior thermodynamic
performance, a CO₂ avoided cost for the CaL retrofits was demonstrated to fall between 10 and 30 €/tCO₂. Such figures demonstrate the economic superiority of the CaL retrofits over chemical solvent scrubbing, which were reported to fall between 35 €/tCO₂ and 110 €/tCO₂. Furthermore, CaL has been used as a foundation of novel processes for low-carbon power generation and hydrogen production, and synthesis of chemicals, such as dimethyl ether and synthetic natural gas.

The ultimate challenge that may influence the viability of CaL in the long-term is the deterioration in the CO₂ capture material performance. Such a deterioration in sorbent performance is commonly considered in the CaL retrofit assessments either as a fixed conversion in the carbonator or via the semi-empirical correlations that combine experimental data and process conditions. In the first approach, the fixed sorbent conversion of about 20%, defined as the ratio of the factual and the maximum amount of CaO converted to CaCO₃, is usually assumed for the natural limestone. In the latter approach, the fresh sorbent make-up of about 5% is commonly considered to arrive at the average sorbent conversion of between 15% and 20%. However, the key challenge of relying on semi-empirical correlations is that these correlations use the experimental data to derive fitting parameters. As identified in the experimental work by Rodriguez et al. and Charitos et al., there are high measurement errors associated with estimating solid flow rates and the average carbonation conversion, resulting from the measurement uncertainty. Consequently, the error associated with using the semi-empirical correlations to estimate the average sorbent conversion can reach ±20%. Such an error in estimating the average sorbent conversion will directly influence the amount of sorbent necessary to achieve desired CO₂ removal level in the carbonator and, thus, the amount of energy necessary for the sorbent regeneration. This, in turn, will affect the efficiency and economic penalties of the CaL retrofit. However, the influence of the uncertainty in the sorbent characteristics on the techno-economic viability of CaL has not been thoroughly examined.

The use of a stochastic method to the techno-economic evaluation of CCUS was shown to result in a more in-depth understanding of the technical and economic risks associated with the viability of CCUS. Rubin and Rao were the first to quantify the uncertainty in the key economic performance indicators of the CFPP retrofitted with chemical solvent scrubbing (monoethanolamine). Using the Integrated Environmental Control Model, they showed that due to uncertainties present in the host plant and the CCUS plant, the levelised cost of electricity (LCOE) could vary between 57 and 139 €/MWh (median 103 €/MWh). In turn, the CO₂ avoided cost could vary between 22 and 96 €/tCO₂ (median 56 €/tCO₂). Hanak and Manovic have quantified the uncertainty in the LCOE of the CFPP retrofitted with CaL. That study revealed that the median value for the LCOE would be 95.6 €/MWh, and varied between 59 and 126 €/MWh. Although the study by Rubin and Rao and Hanak and Manovic were performed for different host plants and under different assumptions, the retrofit of CaL was shown to result in a lower LCOE compared to that of chemical solvent scrubbing. Yet, the study by Hanak and Manovic has not accounted for the uncertainty present in the sorbent characteristics. Roussanaly et al. have compared the retrofit of chemical solvent scrubbing to a waste-to-energy plant. They showed that depending on the solvent used in the process, CCUS retrofits would result in a lower CO₂ avoided cost of 142 €/tCO₂ (range 168-368 €/tCO₂) for chemical solvent scrubbing that uses advanced amine-based solvent and 206 €/tCO₂ (range 115-260 €/tCO₂) for chemical solvent scrubbing that uses monoethanolamine. Such results imply that the characteristics of CO₂ capture material can significantly influence the economic viability of CCUS.

The experimental trials revealed a significant uncertainty in the average sorbent conversion in the carbonator that can reach up to ±20%. Yet, the importance of such uncertainty in the sorbent characteristics has been disregarded in the techno-economic assessments of CaL presented in the current literature, regardless of whether the deterministic or stochastic assessment methods were applied. Consequently, the superior techno-economic performance of the CaL retrofits with respect to other CCUS technologies may have been overestimated. For this reason, this study aims to quantify the impact of uncertainty in the sorbent characteristics on the techno-economic feasibility of the 580 MWₑₛ CFPP retrofitted with CaL. It uses a stochastic approach to techno-economic assessment. Furthermore, it combines a robust surface response approximation model, which was developed using an artificial neural network (ANN), a validated Aspen Plus process model, and the Monte Carlo simulation. Such an analysis will provide an in-depth understanding of the effect of sorbent characteristics (initial conversion and residual conversion) on thermodynamic (net efficiency, carbonation conversion), environmental (specific emissions) and economic (CO₂ avoided cost, LCOE) performance. Moreover, the influence of the key input variables, which describe the statistical distribution of the sorbent characteristics, on the techno-economic feasibility of the CFPP retrofitted with CaL is analysed.
2 METHODS

2.1 Process model description

This study aims to demonstrate the effect of the uncertainty in the average sorbent conversion model on the techno-economic feasibility of the CaL retrofit (Figure 1). The 580 MWₑₚ CFPP was considered as the host plant. It has been represented in Aspen Plus, following the design and operating conditions in the NETL report. A full description of the process model is available in Hanak et al. This model represents a conventional CFPP layout, including the power boiler with NOₓ, SOₓ and fly ash emission control equipment. The heat generated from the combustion of coal in the power boiler is utilised to produce high-pressure live steam (242.3 bar) and reheat steam (45.2 bar) at 593.3°C, which is then used in the steam cycle. The model also comprises a typical steam cycle consisting of high-, intermediate- and low-pressure extraction condensing turbines. In this type of steam turbine, a fraction of the steam is used for feedwater heating before it enters the power boiler. This model comprises four indirect low-pressure feedwater heaters, one mixed feedwater heater (deaerator), and three high-pressure feedwater heaters.

The CaL model considered in this work was described in detail by Hanak et al. It was built in Aspen Plus and validated with the experimental data from the La Pereda pilot plant under different operating conditions. This model considers the semi-empirical correlation by Rodriguez et al. given in Equation (1) to calculate the average sorbent conversion in the carbonator.

\[
X_{ave} = (F_0 + F_Rr_0)f_{calc} \left[ \frac{a_1f_1^2}{F_0 + F_Rf_{carb}f_{calc}(1 - f_1)} \right] + \frac{a_2f_2^2}{F_0 + F_Rf_{carb}f_{calc}(1 - f_2)} + b
\]  

In Equation (1), the maximum average conversion of the sorbent depends on the make-up rate of fresh limestone \(F_0\), the circulation rate of sorbent \(F_R\), the extent of carbonation \(f_{carb}\) and calcination \(f_{calc}\) reactions, a fraction of limestone that was never calcined \(r_0\), and sorbent characteristics \(f_1, f_2, b, a_1, a_2\).

However, the sorbent characteristics in Equation (1) represent the fitting parameters used to map the experimental results. Consequently, these fitting parameters cannot be attributed to any physical quantities that can be measured. Therefore, to better appreciate the influence of uncertainty in the sorbent characteristics on the techno-economic feasibility of the CaL retrofits, the semi-empirical correlation derived by Wang and Anthony and Abanades et al., presented in Equation (2), was used in this work.
\[
X_{\text{ave}} = \frac{X_i (1 - X_r) F_0}{F_0 + F_R (1 - X_i)} + X_r
\] (2)

In this semi-empirical correlation, which was derived based on the second-order deactivation rate for catalyst deactivation via sintering, the sorbent performance is characterised by a residual conversion \(X_r\) and an initial conversion \(X_i\). The former represents the actual carbonation conversion of fresh sorbent. The latter represents the minimum sorbent conversion rate after a high number of calcination-carbonation cycles (i.e., >50). As this correlation allows exploring the uncertainty associated with specific physical characteristics of the sorbent, it was deemed more suitable for this study. It is also important to note that both semi-empirical correlations were commonly used to assess the techno-economic feasibility of large-scale CaL retrofits.

To ensure that the CaL model used in this study remains accurate and representative, the residual conversion \(X_r\) and the initial conversion \(X_i\) in the model by Abanades et al. \(^{36}\) were estimated by minimising the root-square error between the prediction of this model and the model by Rodriguez et al. \(^{34}\) over 50 carbonation-calcination cycles. Table 1 presents the outcome of this fitting exercise. It was shown that the relative error between the thermodynamic (2.7%) and economic performance (2.9%) is less than 3%. Such an outcome indicates that the conclusions made in this study will not be significantly influenced by the selection of the sorbent deactivation model.

### 2.2  Techno-economic metrics

The techno-economic feasibility of the CaL retrofit is assessed considering its net efficiency penalty, specific CO\(_2\) emissions, avoided CO\(_2\) cost and LCOE as the key performance indicators. The net efficiency \(\eta_{\text{null}}\) is defined in Equation (3) as the ratio of the net power output \(W_{\text{net}}\) and the chemical energy input. The latter is estimated as the product of the lower heating value of the fuel and its mass flow rate \(m_{\text{fuel}}\). The net efficiency penalty \(\Delta\eta_{\text{null}}\) is the difference between the net efficiency of the host CFPP without carbon capture and the CaL retrofit, as defined in Equation (4).

\[
\eta_{\text{null}} = \frac{W_{\text{net}}}{m_{\text{fuel}} \times LHV} \times 100\%
\] (3)

\[
\Delta\eta_{\text{null}} = \eta_{\text{null,ref}} - \eta_{\text{null,Cal.}}
\] (4)

The environmental performance of the CaL retrofit is assessed considering the specific CO\(_2\) emissions. This key performance indicator is defined in Equation (5) as the ratio of the CO\(_2\) mass flow rate in the clean gas stream leaving the carbonator \(m_{\text{CO}2}\) and the net power output.

\[
e_{\text{CO2}} = \frac{m_{\text{CO2}}}{W_{\text{net}}}
\] (5)

The economic performance of the CaL retrofit is assessed applying the framework described in detail by Hanak and Manovic. \(^{26,37}\) The LCOE represents a minimum electricity cost for the project to break even, and is defined in Equation (6). Thus, the economic feasibility of the CaL retrofit depends on the net thermal efficiency, capacity factor, the total capital requirement \(\text{TCR}\), specific fuel cost \(\text{SFC}\), variable \(\text{VOM}\) and fixed \(\text{FOM}\) operating and maintenance costs, and fixed charge factor \(\text{FCF}\). The FCF considers the project lifetime \(t\) and the discount rate \(r\), as defined in Equation (7).

\[
\text{LCOE} = \frac{\text{TCR} \times \text{FCF} + \text{FOM}}{W_{\text{net}} \times \text{CF} \times 8760} + \text{VOM} + \frac{\text{SFC}}{\eta_{\text{null}}}
\] (6)

### Table 1 Comparison of the calcium looping performance using different sorbent deactivation models

| Parameter | Rodríguez et al. \(^{34}\) | Abanades et al. \(^{36}\) |
|-----------|-----------------------------|-----------------------------|
| Sorbent characteristic | | |
| Fitting parameter, \(a_1\) [-] | 1.0000 | |
| Fitting parameter, \(f_1\) [-] | 0.7467 | |
| Fitting parameter, \(a_2\) [-] | 0.0861 | |
| Fitting parameter, \(f_2\) [-] | 0.9705 | |
| Fitting parameter, \(b\) [-] | 0.0750 | |
| Residual conversion, \(X_r\) [-] | 0.1112 | |
| Initial conversion, \(X_i\) [-] | 0.7743 | |
| Process conditions | | |
| Make-up rate of fresh limestone, \(F_0\) [kmol/s] | 0.6013 | |
| Sorbent circulation rate, \(F_R\) [kmol/s] | 15.0204 | |
| Carbonation extent, \(f_{\text{carb}}\) [-] | 0.7 | |
| Calcination extent, \(f_{\text{calc}}\) [-] | 0.95 | |
| Maximum sorbent conversion [%] | 23.6 | 21.5 |
| Average sorbent conversion [%] | 15.7 | 14.3 |
| Impact on techno-economic performance | | |
| Net efficiency penalty [% points] | 7.64 | 7.85 |
| Levelised cost of electricity [€/MWh] | 78.18 | 80.48 |
FCF = \frac{r(1+r)^t}{(1+r)^t - 1} \tag{7}

The TCR corresponds to the capital cost required for the CaL unit and the reference CFPP. The former was determined based on the work by Romano et al., whereas the latter was estimated based on the NETL report using the exponential method function, as explained by Hanak et al. The input data to Aspen Plus models and economic assessment models is shared in Supporting Information S1.

2.3 Stochastic modelling

The influence of the uncertainty in the sorbent deactivation model on the techno-economic feasibility of the CaL retrofit was quantified using the stochastic assessment methodology presented in detail by Hanak and Manovic. The uncertainty in the measurement of residual conversion and initial conversion are considered as the key physical characteristics determining the CO₂ capture capacity of the sorbent. Conversely to the approach used by Rubin and Rao, who used the Integrated Environmental Control Model that allows representing any input parameters as probability distribution function rather than deterministic values directly in the model, this study uses a response surface method to generate a robust approximation model to minimise the computational demand associated with the stochastic assessment. The design matrix that maps the performance of CaL retrofit was generated using the Aspen Plus model presented in Section 2.1. The generated data set is used as a basis for developing a robust surface approximation model using ANN. The design matrix comprises 60 data points that represent the performance of the CaL retrofit, considering carbonator conversion, efficiency penalty, LCOE, and specific CO₂ emissions. It was generated by running the Aspen Plus model under different sorbent conditions:

- the initial conversion was varied between 0.60 and 0.85; and
- the residual conversion was varied between 0.02 and 0.20.

The design matrix created to perform this study is shared in Supporting Information S1. These data were used to develop ANN employing the Neural Network Fitting toolbox in Matlab. A two-layer feed-forward ANN architecture was considered. The number of sigmoid neurons in the hidden layer was determined via a sensitivity analysis (Figure 2). For this purpose, the ANN architectures comprising 10, 25, 50, 75 and 100 hidden networks were built using the design matrix. These data were randomly allocated to training, validation and testing samples with the default split of 70%, 15% and 15%, respectively. The Levenberg-Marquardt backpropagation training algorithm with Bayesian regularisation was used to train the ANNs. It was because this training algorithm has been considered suitable for small datasets comprising nonlinear data. It is apparent from Figure 2 that the ANN architecture that comprised a low number of neurons in the hidden layer resulted in a high root mean square error of artificial neural network.
square error (RMSE) for the considered key performance indicators. In addition, the sensitivity analysis showed that using too many neurons also resulted in an increase in RMSE. It was especially the case of the ANN with 100 sigmoid neurons and LCOE. In this case, such a high RMSE can be explained by ANN overfitting that results in a good fit between the prediction of the ANN model and training data but a poor fit between the prediction of the ANN model and test data. Consequently, the ANN model used in this study comprised 75 sigmoid neurons and linear output neurons (Figure 3), as it was found to result in the lowest RMSE and provide the best representation of directional outputs.

Finally, the generated ANN was used in the Monte Carlo simulations to examine the influence of uncertainty in the initial conversion and residual conversion on the key performance indicators. It was achieved by performing 10 000 iterations that involved the random generation of input data based on assumed statistical distributions of input variables. As no statistical data is available to describe the variability of the initial conversion and residual conversion, these parameters were assumed to be uniformly distributed. The initial conversion was assumed to vary between 0.60 and 0.85, whereas the residual conversion was assumed to vary between 0.02 and 0.20.

3 | RESULTS AND DISCUSSION

3.1 | Deterministic assessment

To understand the extent to which the key performance indicators are influenced by the variation in the sorbent properties, represented by the initial conversion ($X_i$) and residual conversion ($X_r$), a comprehensive sensitivity
assessment has been performed as described in Section 2.3. The outcome of this sensitivity analysis is used as the design matrix to build the robust approximation model.

The influence of the variation in the sorbent characteristics on the key performance indicators is presented in Figure 4. Figure 4A shows the correlation between the sorbent characteristics and the average sorbent conversion in the carbonator, defined in Equation (2). For the fixed make-up rate of fresh sorbent, an increase in the residual conversion will increase the average sorbent conversion in the carbonator. A similar trend was observed for an increase in the initial conversion. Consequently, the maximal carbonator conversion can be achieved for high values of both residual conversion and initial conversion. It is worth noting that the sensitivity analysis was performed to map the prediction of the CaL retrofit performance so that a robust and accurate ANN model could be developed.

Achieving high conversion rates of sorbent in the carbonator is crucial to the viability of the CaL retrofit. It is because the quantity of sorbent needed to reach the desired carbon capture rate is reduced at high conversion rates, as is the amount of inert sorbent leaving the carbonator. Consequently, the energy demand for sorbent pre-heating to the calciner operating temperature (900°C) is lower, reducing the oxygen and fuel consumption in the calciner.

Figure 4 presents the techno-economic benefits of increased sorbent conversions. It was shown that the variation in the sorbent conversion could result in a corresponding variation in the net efficiency penalty of the CFPP retrofitted with CaL of between 7% points and 12% points (Figure 4B). Such a significant spread in the net efficiency penalty aligns with data reported in the literature.

Consequently, the estimated LCOE would vary between 70 and 140 €/MWh (Figure 4D). Such an outcome implies that the deterministic models are subject to high uncertainty. A selection of favourable sorbent conditions may lead to unrealistic outcomes of the techno-economic analyses.

It needs to be emphasised that not all performance metrics benefit from an improvement in the average conversion of sorbent in the carbonator. As shown in Figure 4C, an increase in the average sorbent conversion led to an increase in the specific CO₂ emissions. Such a correlation is inverse to the ones presented above. As already discussed, higher average sorbent conversion rates result in less sorbent required in the carbonator. Consequently, less sorbent is sent to the calciner for regeneration, reducing the energy requirement of the CaL retrofit. As the amount of heat available for recovery in CaL directly depends on the energy demand in the calciner, the net power output is lower. With a fixed amount of CO₂ leaving the carbonator and, thus, emitted into the atmosphere, such a drop in the net power output leads to higher specific CO₂ emissions, according to Equation (5).

3.2 | Stochastic assessment

The deterministic assessment presented in Section 3.1 has confirmed that the variation in sorbent properties can significantly influence the techno-economic viability of the CaL retrofit. The Monte Carlo Simulations were performed as explained in Section 2.3 to understand the extent to which the key performance indicators are influenced by the uncertainty in the sorbent properties.

3.2.1 | Effect of uncertainty on average sorbent conversion

Before assessing the influence of uncertainty in the characteristics of sorbent on the techno-economic feasibility of the CFPP retrofitted with CaL, it is pertinent to understand how it influences the average conversion of sorbent in the carbonator. Figure 5 showed that the uncertainty in the sorbent characteristics would result in the average carbonation conversion to vary between 5% and 22%, with the 25th percentile and 75th percentile figures of 10.38% and 16.12%. The median value was 13.36%, which is lower than the carbonator conversion of 20% that is
commonly assumed in the techno-economic assessment in the current literature\textsuperscript{21} and that of 14.30\% estimated using the deterministic model (Table 1). It may imply that the current techno-economic assessments may overestimate the CaL performance and the extent of this overestimation is assessed in the following sections.

3.2.2 | Effect of uncertainty on thermodynamic performance

The efficiency penalty is one of the most commonly used key performance indicators in the assessment of the thermodynamic performance of CCUS. It is because it indicates how much the net efficiency of the host CFPP will reduce due to the CaL retrofit. The influence of the uncertainty in the sorbent characteristics on the net efficiency penalty of the CaL retrofit is shown in Figure 6. It has been shown that the statistical distribution of the net efficiency penalty is asymmetrical with moderate positive skew (Skew = 0.84) and a median of 8.08\% points. This figure is slightly higher than the net efficiency penalty of 7.85\% points estimated using the deterministic approach. It is worth emphasising that the values obtained in the stochastic assessment varied between 7.03\% points and 10.79\% points, with the values for the 25th percentile and 75th percentile of 7.66\% points and 8.70\% points. Furthermore, the kurtosis for the efficiency penalty was 0.08, implying that slightly more data are located in the tail compared to the equivalent normal distribution for which kurtosis is 0. Overall, the outcome of the stochastic assessment indicates that due to the uncertainty in the sorbent properties, the most likely values for the efficiency penalty fall between 7.7\% points and 8.7\% points. Such range is higher than that reported for the CaL retrofits based on the deterministic data (6\%-8\% points\textsuperscript{14}).

Such an outcome implies that the uncertainty in the sorbent characteristics is likely to influence the technical viability of the CaL retrofits compared with other CO\textsubscript{2} capture technologies. It is because the uncertainty associated with sorbent conversion will directly translate into the uncertainty of energy demand for sorbent regeneration in the calciner and the amount of heat available in CaL for electricity production. As explained above, the lower the sorbent conversion, the more inert sorbent is circulated between the carbonator and calciner. Consequently, this increases the energy requirement for sorbent regeneration and the amount of energy available for recovery to produce high-pressure steam and, subsequently, electricity.

3.2.3 | Effect of uncertainty on environmental performance

The specific CO\textsubscript{2} emissions, so-called carbon intensity, is the key performance indicators used in the environmental performance assessment of CCUS retrofits to power generation systems. It is because this metric represents the amount of CO\textsubscript{2} emitted into the atmosphere per unit amount of electricity produced. The influence of the uncertainty in the sorbent characteristics on the specific CO\textsubscript{2} emissions of the CaL retrofit is presented in Figure 7. It was found that this key performance indicator is characterised by an asymmetrical distribution with
negative skew (Skew = -0.96) and a kurtosis of 0.39. The former implies that more data are present in the tail compared to the equivalent normal distribution. The median value was 100.39 gCO₂/kWh, with the 25th percentile and 75th percentile of 95.79 and 103.39 gCO₂/kWh. Such an outcome implies a high likelihood that the specific CO₂ emissions for the CFPP retrofitted with CaL estimated using the stochastic approach will be around the deterministic figure of 101.94 gCO₂/kWh. Therefore, such an analysis has revealed that the uncertainty in the sorbent characteristics will marginally impact the viability of the CaL retrofit from an environmental perspective. It could be explained by a relatively small impact of sorbent characteristics on the process efficiency, as explained in Section 3.2.2.

3.2.4 Effect of uncertainty on economic performance

The economic performance of the fossil-fuel power plants retrofitted with CCUS is often examined considering the LCOE. It is because this metric indicates the discounted lifetime cost of constructing and operating the power generation systems per unit of electricity produced. It also represents the minimum cost that the electricity generated from an integrated CFPP and CaL at which the project would break even over its lifetime.⁴³ The influence of the uncertainty in the sorbent characteristics on the LCOE of the CaL retrofit is presented in Figure 8. The outputs from the stochastic assessment have revealed that the statistical distribution of the LCOE has a high positive skew (Skew = 1.34) and a median of 83.20 €/MWh. Such a figure is 3.4% higher than that estimated using the deterministic approach. Moreover, a high proportion of the generated data is located in the tail compared to the equivalent normal distribution, as can be seen from a high positive value obtained for kurtosis of 1.56. The outputs of the stochastic assessment also revealed that the LCOE for the 25th percentile and 75th percentile was 78.43 and 91.30 €/MWh, respectively. Importantly, if the sorbent performs poorly (worst-case scenario), the LCOE estimated for the CaL retrofit can reach up to 133.71 €/MWh. Such figures are higher than those reported in Section 3.1 (80.48 €/MWh). It implies that the economic assessment using the deterministic approach could underestimate the costs associated with the CaL retrofits. In addition, these figures are higher than those already reported for the CaL retrofits to fossil fuel-fired power plants (50-75 €/MWh).¹⁴

Importantly, as the CO₂ avoided cost is estimated using the LCOE, its statistical distribution was found to have the same descriptive characteristics, such as skew of 1.34 and kurtosis of 1.56. The median CO₂ avoided cost was 35.94 €/tCO₂, and the corresponding 25th percentile and 75th percentile values were 29.74 and 46.50 €/tCO₂, respectively. Although these figures are significantly lower than the current EU-ETS prices of about 60 to 90 €/tCO₂,⁴⁴ these are higher than the figures of 10 to 30 €/tCO₂ reported for the CaL retrofits¹⁴ and 32.40 €/tCO₂ reported in Section 3.1.

It was shown that uncertainty in the sorbent characteristics significantly influences the economic performance of the CaL retrofits. Importantly, a reduction in the average sorbent conversion substantially impacts the LCOE. The stochastic assessment shown in this study revealed that the median value for the average sorbent conversion in the carbonator was 13.36%. Such a figure is significantly lower than 20%, which was commonly assumed by most of the CaL retrofits evaluated in the current literature.²¹ It was also lower than the averages sorbent conversion of 14.30% estimated using the deterministic model described in Section 2. Such results imply that the economic assessments presented in the current literature may underestimate the CO₂ avoided cost and the LCOE of the CaL retrofits.

3.3 Implications on process feasibility

The stochastic assessment results presented in Section 3.2 have indicated that the techno-economic feasibility of the CaL retrofits is highly influenced by the uncertainty in the sorbent characteristics, compared to the outcomes of the deterministic assessment. Table 2 presents a comparison of the deterministic and stochastic key performance
indicators for the CaL retrofit to the CFPP. It can be noted that the uncertainty in the sorbent characteristics can result in lower average sorbent conversions than those commonly assumed in the deterministic models. This directly translates to higher net efficiency penalties, LCOE and CO₂ avoided cost of the CaL retrofits.

It needs to be emphasised that although the median values for the key performance indicators appear to be only slightly worse than those generated in the deterministic models, the detailed analysis presented in Section 3.2 implies that a significant amount of data falls in the tail of the generated statistical distributions. Considering the 75th percentile, which indicates that the selected key performance indicator will be equal or lower to a given value with a 75% probability, it can be seen that the stochastic data presents a more conservative performance of the CaL process.

It needs to be stressed that the predictions obtained via the stochastic assessment depend on the assumed statistical distribution of the stochastic variables. It is,

| Key performance indicator                  | Deterministic | Stochastic |
|--------------------------------------------|---------------|------------|
| Average sorbent conversion [%]             | 14.30         | 10.38      |
|                                            |               | 13.36      |
|                                            |               | 16.12      |
| Net efficiency penalty [% points]         | 7.85          | 7.66       |
|                                            |               | 8.08       |
|                                            |               | 8.70       |
| Specific CO₂ emissions [gCO₂/kWh]         | 101.94        | 95.79      |
|                                            |               | 100.39     |
|                                            |               | 103.39     |
| Levelised cost of electricity [€/MWh]     | 80.48         | 78.43      |
|                                            |               | 83.20      |
|                                            |               | 91.30      |
| CO₂ avoided cost [€/tCO₂]                 | 32.40         | 29.74      |
|                                            |               | 35.94      |
|                                            |               | 46.50      |
reveals that such a variation will have a relatively strong influence on the average conversion in the carbonator. A ±10% variation in the assumed distribution for the maximum value of the initial conversion \(X_{i,\text{max}}\) was shown to result in the variation in the average carbonator conversion between −10.0% (a 10% reduction in \(X_{i,\text{max}}\)) and +12.5% (a 10% increase in \(X_{i,\text{max}}\)). A corresponding variation in the minimum value of the initial conversion \(X_{i,\text{min}}\) and the maximum value of the residual conversion \(X_{r,\text{max}}\) was shown to have a small influence (<4.5%) on the carbonator conversion. The minimum value of the residual conversion \(X_{r,\text{max}}\) had a negligible influence on the carbonator conversion. Furthermore, Figure 9C reveals that a ±10 variation in the assumed distributions has a negligible influence on the specific CO2 emissions that varied by less than 2.0%. Similarly, such a variation had a small influence (<4.0%) on the variation in the median value estimated for efficiency penalty (Figure 9B) and LCOE (Figure 9D).

4 | CONCLUSIONS

This study aimed to quantify the impact of uncertainty in the sorbent characteristic on the techno-economic feasibility of the CaL retrofit to the 580 MWel CFPP. This was achieved using a stochastic approach to techno-economic assessment that integrates detailed process modelling and economic assessment, surface response approximation models based on ANNs, and Monte Carlo simulation.

The outputs from the stochastic assessment revealed that a median of the carbonator conversion was 13.36%, which was nearly 1% point lower than that estimated using the deterministic model. It was also significantly lower than the average carbonator conversion of 20%, which is commonly assumed in the techno-economic feasibility assessments of the CaL retrofits. As the average sorbent conversion in the carbonator directly influences the amount of sorbent circulated between the CaL reactors and limestone make-up required, this study showed that the current techno-economic assessments may underestimate the energy and economic implications of the CaL retrofits.

First, the most likely values for the efficiency penalty were shown to fall between 7.7% points and 8.7% points (25th and 75th percentile, respectively), with a median of 8.08% points. Such a figure is higher than the figure determined using the deterministic approach (7.85% points) and the figures reported for the CaL retrofits of 6% to 8% points in the current literature. Second, the stochastic analysis revealed that the uncertainty in the sorbent characteristics will have a significant impact on the environmental performance of the CaL retrofit. The median value for the specific CO2 emissions was estimated to be 100.39 gCO2/kWh, and was shown to vary between 95.79 and 103.39 gCO2/kWh (25th and 75th percentile, respectively). Such figures are close to that estimated in the deterministic assessment (101.94 gCO2/kWh). Third, the stochastic assessment presented in this study revealed that the uncertainty in the sorbent characteristics will have a significant influence on the economic feasibility of the CaL retrofits. Namely, the most likely figures for the LCOE were estimated to be 78.43 to 91.30 €/MWh (25th and 75th percentile, respectively), with the median of 83.20 €/MWh. Furthermore, the CO2 avoided cost was reported to be 29.74 to 46.50 €/tCO2, with a median of 35.94 €/tCO2. Such figures are higher than those obtained from the deterministic assessment (80.48 €/MWh and 32.40 €/tCO2), implying that the economic assessment using the deterministic approach could underestimate the costs associated with the CaL retrofits. Finally, it was shown that the ±10% variation in the key input parameters that represent the statistical distributions of the sorbent initial conversion and residual conversion had a small influence on the predicted median values.

A comparison of the key performance indicators generated based on a deterministic and stochastic approach confirmed that the uncertainty in the sorbent characteristics will influence the techno-economic feasibility of the CaL retrofits. This is especially important in the assessment of economic viability. With other assumptions being equal, the stochastic assessment resulted in the median values for the CO2 avoided cost and LCOE higher by 10.93% and 3.38% than those determined using the deterministic assessment, respectively. Therefore, it can be concluded that using the stochastic approach in the techno-economic assessment of CCUS can provide more in-depth insights into technology viability and enable more-informed investment decisions.

Finally, it is crucial to note that this work focused solely on assessing the influence of the uncertainty in the sorbent characteristics on the techno-economic viability of the CaL retrofits. It was performed based on the assumption that other thermodynamic and economic assumptions remain constant, which can be seen as a limitation of this study. Moreover, the assessment of the environmental performance included only process level CO2 emissions and, thus, did not consider the process life-cycle emissions. Therefore, the future work will
present a stochastic assessment of integrated techno-economic and environmental assessment of the CaL retrofit.

ENDNOTE
* Economic indicators recalculated from USD to EUR considering 2002 USD/EUR exchange rate of 0.95.

DATA AVAILABILITY STATEMENT
Data available in article supplementary material.

ORCID
Dawid P. Hanak https://orcid.org/0000-0002-1069-8815

REFERENCES
1. IPCC. Climate Change 2022: Impacts, Adaptation and Vurnerability. Switzerland: Intergovernmental Panel on Climate Change; 2022.
2. IEA. The Role of CCUS in Low-Carbon Power Systems – Analysis. France, Paris: International Energy Agency; 2020.
3. UN. Adoption of the Paris Agreement. France, Paris: United Nations Framework Convention on Climate Change; 2015.
4. Capocelli M, De Falco M. Generalized penalties and standard efficiencies of carbon capture and storage processes. Int J Energy Res. 2022;46:4808-4824. doi:10.1002/er.7474
5. IEA. Energy Technology Perspectives 2020. Paris, France: International Energy Agency; 2020.
6. Bui M, Zhang D, Fajardy M, Mac Dowell N. Delivering carbon negative electricity, heat and hydrogen with BECCS – comparing the options. Int J Hydrogen Energy. 2021;46:15298-15321. doi:10.1016/j.ijhydene.2021.02.042
7. Murele OC, Zulkafl NJ, Kopanos G, Hart P, Hanak DP. Integrating biomass into energy supply chain networks. J Clean Prod. 2020;248:119246. doi:10.1016/j.jclepro.2019.119246
8. Abdul Manaf N, Qadir A, Abbas A. Temporal multiscalar decision support framework for flexible operation of carbon capture plants targeting low-carbon management of power plant emissions. Appl Energy. 2016;169:912-926. doi:10.1016/j.apenergy.2016.02.052
9. IEA. CCUS in Power. Paris, France: International Energy Agency; 2021. https://www.iea.org/reports/ccus-in-power
10. Romeo LM, Minguell D, Shirmohammadi R, Andrés JM. Comparative analysis of the efficiency penalty in power plants of different amine-based solvents for CO2 capture. Ind Eng Chem Res. 2020;59:10082-10092. doi:10.1021/acs.iecr.0c01483
11. Žalec D, Hanak DP, Može M, Golobič I. Process development and performance assessment of flexible calcium looping biomass gasification for production of renewable gas with adjustable composition. Int J Energy Res. 2022;46:6197-6215. doi:10.1002/er.7558
12. Shimizu T, Hirama T, Hosoda H, Kitano K, Inagaki M, Tejima K. A twin fluid-bed reactor for removal of CO2 from combustion processes. Chem Eng Res Design. 1999;77:62-68. doi:10.1205/026387699525882
13. Romeo LM, Abanades JC, Escoa JM, et al. Oxyfuel carbonation/calcination cycle for low cost CO2 capture in existing power plants. Energ Conver Manage. 2008;49:2809-2814. doi:10.1016/j.enconman.2008.03.022
14. Hanak DP, Michalski S, Manovic V. From post-combustion carbon capture to sorption-enhanced hydrogen production: a state-of-the-art review of carbonate looping process feasibility. Energ Conver Manage. 2018;177:428-452. doi:10.1016/j.enconman.2018.09.058
15. Pillai BBK, Surywanshi GD, Patnaikuni VS, Anne SB, Vooradi R. Performance analysis of a double calcium looping-integrated biomass-fired power plant: exploring a carbon reduction opportunity. Int J Energy Res. 2019;43:5301-5318. doi:10.1002/er.4520
16. Pillai BBK, Surywanshi GD, Patnaikuni VS, Anne SB, Vooradi R. A novel calcium looping-integrated NGCC power plant configuration for carbon capture and utilization—comprehensive performance analysis. Int J Energy Res. 2022;46:900-922. doi:10.1002/er.7212
17. Du Y, Gao T, Rochelle GT, Bhowm AS. Zero- and negative-emissions fossil-fired power plants using CO2 capture by conventional aqueous amines. Int J Greenh Gas Control. 2021;111:103473. doi:10.1016/j.ijggc.2021.103473
18. Rubin ES, Davison JE, Herzog HJ. The cost of CO2 capture and storage. Int J Greenh Gas Control. 2015;40:378-400. doi:10.1016/j.ijggc.2015.05.018
19. Hanak DP, Michalski S, Manovic V. Supercritical CO2 cycle for coal-fired power plant based on calcium looping combustion. Thermal Sci Eng Prog. 2020;20:100723. doi:10.1016/j.tsep.2020.100723
20. Tregambi C, Bareschino P, Hanak DP, Montagnaro F, Pepe F, Mancusi E. Modelling of an integrated process for atmospheric carbon dioxide capture and methanation. J Clean Prod. 2022;356:131827. doi:10.1016/j.jclepro.2022.131827
21. Hanak DP, Anthony EJ, Manovic V. A review of developments in pilot plant testing and modelling of calcium looping process for CO2 capture from power generation systems. Energy Environ Sci. 2015;8:2199-2249. doi:10.1039/C5EES00228G
22. Kunze C, De S, Slipeff H. A novel IGCC plant with membrane oxygen separation and carbon capture by carbonation-calcinations loop. Int J Greenh Gas Control. 2011;5:1176-1183. doi:10.1016/j.ijggc.2011.05.038
23. Hanak DP, Biliyok C, Anthony EJ, Manovic V. Modelling and comparison of calcium looping and chemical solvent scrubbing retrofits for CO2 capture from coal-fired power plant. Int J Greenh Gas Control. 2015;42:226-236. doi:10.1016/j.ijggc.2015.08.003
24. Martínez A, Lara Y, Lisbona P, et al. Operation of a cyclonic preheater in the Ca-looping for CO2 capture. Environ Sci Tech. 2013;47:11335-11341. doi:10.1021/es401601k
25. Rodríguez N, Alonso M, Abanades JC. Experimental investigation of a circulating fluidized-bed reactor to capture CO2 with CaO. AIChE J. 2011;57:1356-1366. doi:10.1002/aic.12337
26. Charitos A, Rodríguez N, Hawthorne C, et al. Experimental validation of the calcium looping CO2 capture process with two circulating fluidized bed carbonator reactors. Ind Eng Chem Res. 2011;50:9685-9695. doi:10.1021/ie200579f
27. Rubin ES, Rao AB. Uncertainties in CO2 capture and sequestration costs. In: Kay JG, ed. Greenhouse Gas Control Technologies - 6th International Conference. Oxford: Pergamon; 2003:1119-1124. doi:10.1002/B978-008044276-1.50177-X
28. Hanak DP, Manovic V. Economic feasibility of calcium looping under uncertainty. Appl Energy. 2017;208:691-702. doi:10.1016/j.apenergy.2017.09.078
29. Roussanaly S, Ouassou JA, Anantharaman R, Haaf M. Impact of uncertainties on the design and cost of CCS from a waste-to-energy plant. Front Energy Res. 2020;8. doi:10.3389/fenrg.2020.00017
30. Hanak DP, Biliyok C, Manovic V. Efficiency improvements for the coal-fired power plant retrofit with CO2 capture plant using chilled ammonia process. Appl Energy. 2015;151:258-272. doi:10.1016/j.apenergy.2015.04.059
31. Hanak DP, Biliyok C, Manovic V. Rate-based model development, validation and analysis of chilled ammonia process as an alternative CO2 capture technology for coal-fired power plants. Int J Greenh Gas Control. 2015;34:52-62. doi:10.1016/j.ijggc.2014.12.013
32. Black J. Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity. National Energy Technology Laboratory: Pittsburgh, PA; 2013.
33. Sánchez-Biezma A, Paniagua J, Díaz L, et al. Testing postcombustion CO2 capture with CaO in a 1.7 MWt pilot facility. Energy Procedia. 2013;37:1-8. doi:10.1016/j.egypro.2013.05.078
34. Rodríguez N, Alonso M, Abanades JC. Average activity of CaO particles in a calcium looping system. Chem Eng J. 2010;156:388-394. doi:10.1016/j.cej.2009.10.055
35. Wang J, Anthony EJ. On the decay behavior of the CO2 absorption capacity of CaO-based sorbents. Ind Eng Chem Res. 2005;44:627-629.
36. Abanades JC, Anthony EJ, Wang J, Oakey JE. Fluidized bed combustion systems integrating CO2 capture with CaO. Environ Sci Tech. 2005;39:2861-2866. doi:10.1021/es0496221
37. Hanak DP, Manovic V. Calcium looping combustion for high-efficiency low-emission power generation. J Clean Prod. 2017;161:245-255. doi:10.1016/j.jclepro.2017.05.080
38. Romano MC, Spinelli M, Campanari S, et al. The calcium looping process for low CO2 emission cement and power. Energy Procedia. 2013;37:7091-7099. doi:10.1016/j.egypro.2013.06.645
39. NETL. 2012 Technology Readiness Assessment - Overview. Pathway for Aiding the Next Generation of Affordable Clean Energy Technology - Carbon Capture, Utilization, and Storage (CCUS) FutureGen Alliance FutureGen Alliance FutureGen Alliance. Pittsburgh, PA: National Energy Technology Laboratory; 2012.
40. Hanak DP, Erans M, Nabavi SA, Jeremias M, Romeo LM, Manovic V. Technical and economic feasibility evaluation of calcium looping with no CO2 recirculation. Chem Eng J. 2018;335:763-773. doi:10.1016/j.cej.2017.11.022
41. Chu J, Liu X, Zhang Z, Zhang Y, He M. A novel method overcoming overfitting of artificial neural network for accurate prediction: application on thermophysical property of natural gas. Case Stud Thermal Eng. 2021;28:101406. doi:10.1016/j.csite.2021.101406
42. Perejón A, Romeo LM, Lara Y, Lisboa P, Martínez A, Valverde JM. The Calcium-Looping technology for CO2 capture: on the important roles of energy integration and sorbent behavior. Appl Energy. 2016;162:787-807. doi:10.1016/j.apenergy.2015.10.121
43. Papapetrou M, Kosmadakis G. Chapter 9 - Resource, environmental, and economic aspects of SGHE. In: Tamburini A, Cipollina A, Micale G, eds. Salinity Gradient Heat Engines. Duxford, England: Woodhead Publishing; 2022:319-353. doi:10.1016/B978-0-08-102847-6.00006-1
44. Carbon Price Viewer. Ember. 2022. https://ember-climate.org/data/carbon-price-viewer/. Accessed July 15, 2022.

**SUPPORTING INFORMATION**

Additional supporting information can be found online in the Supporting Information section at the end of this article.

**How to cite this article:** Hanak DP. Effect of uncertainty in sorbent characteristic on techno-economic feasibility of carbonate looping for decarbonisation of coal-fired power plant. Int J Energy Res. 2022;46(12):17441-17454. doi:10.1002/er.8412