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Retrofitting of Cement Plant with Carbon Capture Technology and Emissions Trading Scheme (ETS): An Integrated P-Graph and AHP Approach

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Cement manufacturing is an energy-intensive industry and is the third largest greenhouse gas (GHG) emitter accounting for 8 % of the world's total emissions. There are mitigations to limit its carbon footprint through process optimization and using alternatives to fossil-derived fuels. Another technological option to meet the higher carbon dioxide (CO₂) reduction target is carbon capture. The post-combustion process is considered the most straightforward and widely studied among carbon capture technologies (CCTs) in advanced stages of development for industrial application. However, the progress of CCTs on an industrial scale has been hindered by low profitability due to the high capital necessary to upscale the technology and retrofit industrial plants. Sales from utilizing the captured CO₂ and carbon taxing and trading benefit the application of these technologies. This paper proposes a methodology built from the P-graph and Analytical Hierarchy Process (AHP) to aid in the planning of retrofitting cement plants with post-CCTs in a cap-and-trade environment utilizing an Emissions Trading Scheme (ETS). Three alternative post-combustion technologies were considered, namely monoethanolamine (MEA) absorption technology, chilled ammonia process (CAP), and membrane-assisted liquefaction (MEM). The criteria used to prioritize alternatives are the net CO₂ avoided, profitability, and the retrofitability of the technology to an existing plant. The results suggest that CAP is the most profitable based on P-graph calculation. However, MEA is the most optimal network considering the importance of net CO2 avoided and the level of retrofitability. Further sensitivity analysis of the model shows that CAP is the most applicable technology once the profitability score exceeds 0.8341. CAP and MEA will have an equal ranking at a retrofitability score of 0.0632. More than this score, the latter outranked the other two technologies. Finally, MEM surpassed CAP and MEA at a minimum net CO₂ avoided score of 0.7079.

1. Introduction

Cement is considered one of the essential materials in the civil engineering and infrastructure building industry. No potential substitute can compete with its functional capacity, leading to its continuously growing production worldwide (Miller et al., 2021). However, the cement manufacturing industry is the third largest emitter, accounting for about 8 % of the world's total GHG emissions. It is estimated that one kilogram of CO₂ is generated for every kilogram of cement produced, equivalent to 3 to 4 Gt CO₂ annually when summed up. This amount is projected to grow as infrastructure projects are expected to double by 2060 (Chandler, 2019). To address this environmental issue inherent to the chemistry of producing clinker from limestone as the primary raw material of cement, the industry employs practices to reduce its carbon footprint, including process optimization and utilizing alternatives to fossil-derived fuels. Additionally, per Paris Agreement that set an increased emission reduction target to help fight climate change by limiting global warming to 1.5 °C, the International Energy Agency (EIA) included carbon capture as a technological option for industries' decarbonization (Zhang et al., 2020).

CCTs considered for industrial application include post-combustion capture, pre-combustion capture, oxyfuel combustion, and electrochemical separation (Luis, 2016). Among these types, the post-combustion process, which usually adapts aqueous amine solutions, including monoethanolamine (MEA), is regarded as the most widely applied and straightforward process on a global scale. This method remains the only applicable CO₂

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capture to existing large power plants capable of significant emission reduction (Raganati et al., 2021). In the post-combustion process, the amine solution will be brought in contact with effluent gas generated by fuel combustion to absorb the CO₂, allowing exhaust gas of nitrogen and oxygen mixture to be released into the atmosphere (Basile et al., 2011). Though the MEA solvent process is the most extensive, it requires a high solvent regeneration energy use (Luis, 2016), making the identification of potential alternatives of utmost importance. One of the alternatives is the Chilled Ammonia Process (CAP), a solvent-based regenerable process utilizing aqueous ammonium solution to form ammonium carbonate leading to CO₂ capture (Kozak et al., 2009). Employing ammonia in CO₂ capture results in significantly lower absorption heat of CO₂ relative to amines, reducing the risk of degradation problems while achieving a higher volume of CO₂ collected (Darde et al., 2010). Another post-combustion process to capture CO₂ is through membrane technology which has earned the interest of various studies for its efficiency, ease of installation, energy-saving features, operational flexibility, and the least required use of chemicals (Chen et al., 2022).

When deploying CCTs, the Process Synthesis Network (PNS), Multiple Criteria Decision Analysis (MCDA) techniques, and mathematical modeling are tools that can aid in decision-making. The P-graph framework that tackles PNS problems can promote network design and optimization in CO₂ capture, transport, storage, utilization, and hostile emission technology networks. Though this tool can provide optimal and near-optimal solutions for selecting technologies to deploy and utilization pathways, only a few publications employ this software (Migo-Sumagang et al., 2022). CO₂ capture and its utilization selection can be more efficient with the help of decision analysis tools, including AHP, in the scheduling approach for optimized source and sinks matching through mathematical models. AHP subdivides complex decision-making into certain levels and arranges it in hierarchic order to which a pairwise comparison scheme is applied. This problem-structuring method provides an efficient framework for determining several critical decisions. It became a valuable tool for problems involving multi-criteria considerations, including prioritization, resource allocation, and determining optimum alternatives (Saaty, 2005). Tapia et al. (2017) proposed CO₂ utilization options through the AHP-Data Envelopment Process to determine site efficiencies. Wang et al. (2022) developed a carbon management network for region-wide source-sink models through mixed integer nonlinear programming (MINLP).

Despite the significant advancement and high potential of CCTs to mitigate industrial emissions, their development for actual industrial use is slowed down by their low economic viability due to the high capital necessary to upscale and retrofit existing industrial plants. Instead of storing the captured CO₂, the profit from many utilizations of CO₂, together with various economic schemes like carbon taxing and trading that put a cap on emissions allowed, are seen to offset and improve the economic viability of applying these technologies. Kyoto Protocol clean development mechanism mentioned carbon trading as a means to regulate GHG emissions of participating countries. Emission trading is an economic activity involving the selling or buying of environmental services. Those polluters that release more than what is allowed must purchase rights to emit CO₂ to offset their excess emissions (Pandey et al., 2018). The captured CO₂ can be utilized in ethylene, methanol, urea production, beverage carbonation, and enhanced oil recovery. Ethylene production requires 2.5 t of CO₂ (Berkelaar et al., 2022), methanol production needs 1.38 t of CO₂ (Dimian et al., 2019), and urea production demands 0.73 t of CO_2 (Koohestanian et al., 2018). On the other hand, 1.5 g to 5 g of CO_2 is needed per 1 L of the soft drink's carbonation (Kregiel, 2015), while 1 t of CO2 is required to extract 2 bbl to 3 bbl of oil through the enhanced oil recovery process (NETL, 2020). To our knowledge, the combined approach of P-graph and AHP for the evaluation of CCTs' retrofitability, profitability, and environmental impact in cement manufacturing to attain sustainable production while promoting other potential means to improve the revenue, such as ETS and CO₂ utilization has not been reported in the literature.

BAU	Emission Scenarios		
Cement	No limit Total Carbon I	Emission	
Process Cap-and-Trade	No CCT Emission Cap/Limit With CCT Uncep Captured CO2 Center CO2	Deficit CO ₂ credits p <u>recording</u> Excess CO ₂ credits selling of carbon selling of carbon	on credits Carbon Trading / ETS Carbon Utilization Carbonetd Drinks Carbon Utilization Carbonetd Drinks Car

Figure 1: Cement plant emission scenarios from BAU to operating in a cap-and-trade framework

2. Methodology

Figure 1 presents the emission scenarios of a cement plant from business as usual (BAU) where there are no emission limits to how it will operate with a cap-and-trade economic framework where an ETS is available. The selection of CCT for retrofitting a cement plant and its profitability attributed to CO₂ selling, taxing, and trading

are evaluated using a P-graph. Feasible solutions generated by the latter are further evaluated with AHP considering additional criteria relevant to environmental safety and process applicability.

2.1 Process Network Synthesis

The P-graph network is formulated using P-graph Studio version 5.2.4.3 to simulate a particular case of a cement plant retrofitted with a CCT to be selected among three identified technologies to operate with ETS. The CCTs employed are MEA absorption, membrane-assisted CO₂ liquefaction (MEM), and Chilled Ammonia Process (CAP) to attain a sustainable and profitable network with maximized profit. The process network shows the raw materials, electricity, and heat used in cement manufacturing. The CO2-rich flue gas contains the carbon emission of the process. At the same time, the waste heat is sequestered to produce power to be further utilized in the carbon capture process and contain carbon dioxide from entering the atmosphere. The flue gas is connected to three CCTs to select from, requiring external combined steam and power sources for MEA and CAP to utilize the available waste heat from the cement process. MEM does not need steam. To simplify retrofitting an existing plant, no additional facility to produce combined heat and power will be used in this model, and an external power source will be used. The captured CO₂ from the flue gas is designed for utilization and is sold for industrial use at 43,000 ₱/t. The carbon footprint streams for the use of additional power and steam of each CCT are added to account for the final carbon emission of the cement plant with CCT retrofit but not in the total carbon captured, which is based on CCT separation efficiency of 90 %. Cap-and-trade framework considering the significant reduction in carbon emission when a CCT is installed will allow the plant to sell the excess carbon credits for 800 P/t to other entities through ETS and consequently buy credits for 1,100 P/t when the company chooses not to retrofit. Both carbon trading and utilization are expected to contribute to the network's total profit in addition to the revenue generated by the primary product, cement. The ABB algorithm generates the solutions.

2.2 Analytical Hierarchy Process

The solutions generated from P-graph are evaluated using the SuperDecisions V.3.2.0 software considering the network's net CO₂ avoided, profitability, and retrofitability to identify which among the three selected CCTs is the most ideal for retrofitting. This evaluation process is shown in Figure 2 using the following criteria. Net CO₂ avoided accounts for direct emissions from the use of additional utilities. In contrast, the indirect emission is from energy requirements to power the additional equipment and the combined heat and power plant to supply steam for a specific technology compared to the reference plant without capture technology. Profitability refers to the plant's revenue from carbon capture utilization and trading and cement manufacturing less all the cost of production and raw materials. Lastly, retrofitability pertains to the adaptability of the technology to an existing plant considering the maturity of technology, level of experience in the industry, the introduction of new chemicals and subsystems, utilities and services, and impact on cement production. To assess the relevance of these criteria, four valid responses were gathered from industry experts, including plant production personnel, cement industry consultants, and a sustainability performance manager with years of experience ranging from 7 to 49 y at an average of around 24 y across all respondents. Further evaluation of how varying criteria' importance will affect the technology selection is done through AHP sensitivity analysis for each criterion.



Figure 2: MCDA framework for the selection from three CCTs

3. Results and discussion

The P-graph generated seven optimal networks. The maximal structure and the most optimal solution with CAP incorporating CO_2 utilization and trading are presented in Figure 3. The next near-optimal solution is CAP with utilization, followed by alternating with and without trading for MEA and MEM, as shown in Table 1. As expected, a cement plant without retrofit operating in a cap-and-trade framework is considered the least revenue-generating network, with about five times less profit than the top network solution. This is due to the significant contribution of CO_2 utilization and carbon trading incorporated in the system, which is made possible by retrofitting the latter with CCTs. Carbon utilization generated revenue through the assumption that this material can be used by other industries to manufacture their goods. Carbon trading resulted in additional profit,

considering the opportunity it may provide for the administration to sell the excess carbon credits to other carbon emitters at a reasonable expense and compensation.



Figure 3: (a) Maximal structure and most optimal solution (b) of the cement plant retrofitted with CCT and ETS

Feasible Network	Description	Profit, ₱	
Structure 1	CAP with Utilization and Trading	25,077,000,000	
Structure 2	CAP with Utilization	24,970,300,000	
Structure 3	MEA with Utilization and Trading	23,752,600,000	
Structure 4	MEA with Utilization	23,683,100,000	
Structure 5	MEM with Utilization and Trading	23,031,300,000	
Structure 6	MEM with Utilization	22,900,100,000	
Structure 7	No Retrofit	5,385,970,000	

Table 1: Feasible networks generated through the P-graph ABB algorithm with their respective profits



Figure 4: Raw materials, heat, power consumption, and CO₂ emission of CCTs in the seven solution networks

Figure 4 shows the raw material, total energy consumption, and the additional carbon emission of the CCTs of the seven solution networks. Only the network without a retrofit (S7) needs to purchase carbon credits to suffice the deficit necessary to emit CO₂ without having to incur a penalty in terms of legal regulations or to reduce production to meet the emission cap. MEA technology consumes the most combined energy from steam, heat, and electricity, followed by CAP technology and MEM, as it has no steam requirements. The model network of the P-graph is designed to generate solutions with, at most, one CCT selection of the same capture efficiencies and reference plant cement production capacity. As a result, the same heat and raw materials consumption is required to produce cement.

Employing the pairwise comparison results of the criteria, MEA is the most optimal network, followed by CAP and MEM consecutively, as presented in Table 2. Further sensitivity analysis shown in Figure 5 (a) indicates that when profitability exceeds a pairwise comparison score of 0.8341, CAP will surpass MEA and MEM,

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considering that this network possesses the highest revenue. No significant changes will occur at the alternatives ranking with the considerable variation in retrofitability except that MEA and MEM will have an equal ranking at 0.0238 pairwise comparison score. The same scenario will happen for CAP and MEA if retrofitability is given a score of 0.0632, as shown in Figure 5 (b). However, more than this score, the ranking will be almost equally applicable when net CO₂ is given a criteria importance of around 0.6658 to 0.7079. Less than the range, MEA is the top network, followed by CAP and MEM consecutively; however, more than the range, MEM will surpass MEA and CAP.

Table 2: AHP anal	lvsis of the CC1	⁻ considerina profitabi	litv. level of retro	fitability, and net CO ₂ ave	bided
		eeneraening prentaion			

			Criteria			
CC Technology	Profitability P	/y Re	etrofitability N	Net CO ₂ avoi	ded t/y	Ideal Scores
		Pa	airwise comparison			
CAP	25,077,00	0,000	0.2402	622,175	.31	0.9085
MEA	23,752,60	0,000	0.5500	574,385	.96	1.0000
MEM	23,031,30	0,000	0.2098	649,771	.40	0.8645
Pairwise comparison	0.539	6	0.1634	0.297	0	
1		1			1	
0.9		0.9			0.9	
0.7		0.8			0.7	
0.6		0.6			0.6	
0.5		0.5			0.5	
0.4		0.4			0.4	
0.3		0.3			0.2	
0.102	7 0 8 0 9 1	0.2	20204050607080	a 1	0.1, 0.2, 0.3	0.4 0.5 0.6 0.7 0.8 0.9 1
Fy	periments	0.10	Evperime	nts	+	Experiments
CAP 2	0.341	CAP 1	0.3	338	CAP 2	0.333
MEA 1	0.341	MEA 2	0.3	338	MEA 3	0.332
MEM 3	0.317	MEM 3	0.3	324	MEM 1	0.335
Matrix: Goal Profitability 0.834144	04888032334	Matrix: Go	al Retrofitabil 0.06324512423606	7332	Matrix: Goal Net	CO2 Av 0.70785297266452218

Figure 5: Sensitivity analysis using SuperDecisions version 3.2.0 with respect to (a) profitability, (b) retrofitability, and (c) net CO_2 avoided

4. Conclusion

Post-combustion CCTs, including CAP, MEA, and MEM, significantly decrease the carbon footprint of the cement manufacturing industry while optimizing the company's profit generation by initiating other revenue sources like carbon credits trading and captured carbon utilization process. For the presented case, using CAP with carbon trading and utilization is considered the most optimized network with the highest profit generated. Contrariwise, upon the introduction of net CO₂ avoided and retrofitability as the other significant criteria in selecting the CCTs, considering the point of view of the experts in the cement manufacturing plant, MEA offers the most advantageous solution for retrofitting a cement plant. However, ranking is still susceptible to variation depending on how the relevance weights will be distributed among the criteria. Although the integrated P-graph and AHP model suggested CAP and MEA, the applicability of the technologies will depend on a particular management priority with additional factors including material availability, machine retrofitability, allotted budget, and long-term maintenance and effect to consider. This work applies to developed countries and countries with emerging economies promoting sustainable production with a mitigation plan to control their pollution. The case was designed to be applicable to the scenario in the Philippines, where a cap-and-trade framework can soon be introduced. Being a developing country where there are existing cement manufacturing plants with increasing production and forecasted to continue growing in the following years, the feasibility of this design is considerably high. The applicability of the methodology applied, which is P-graph utilization to generate the networks evaluating its profitability and subsequent employment of AHP for further selection process considering various relevant factors for the feasibility analysis and decision making of different CO₂-generating processes such as power stations and industrial plants are beneficial and potential future studies to consider.

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