



PrometheanParticles™

Nanomaterials **reimagined**

BEYOND CO₂ UPTAKE

DETERMINING THE INDUSTRIAL VIABILITY OF METAL-ORGANIC FRAMEWORKS (MOFs) FOR CARBON CAPTURE AND STORAGE (CCS) APPLICATIONS

April 2023



EXECUTIVE SUMMARY

MOF-BASED CARBON CAPTURE CONTINUES TO ADVANCE AT AN EXHILARATING PACE. THE CO₂ UPTAKE PERFORMANCE OF VARIOUS MOFs GENERATES HEADLINES BUT IS ONLY ONE FACTOR TO BE CONSIDERED IN DETERMINING VIABLE CCS CANDIDATE MATERIALS AT INDUSTRIAL SCALE. THIS WHITE PAPER WAS PREPARED TO HELP GUIDE FUTURE MOF DEVELOPMENT AND TO HELP CCS SYSTEM DESIGNERS MORE EFFECTIVELY CHOOSE APPROPRIATE MOF MATERIALS FOR THEIR APPLICATION.

Carbon capture is increasingly being recognised as a critical technology in the range of solutions needed to effect decarbonisation and help limit climate change. The UK government, the German government, and the Intergovernmental Panel on Climate Change (IPCC) have all recently opined that carbon dioxide (CO₂) removal and carbon capture are necessary for the world to have any chance of limiting global warming to the 1.5 °C goal established in the Paris Agreement [1].

Current technological options for CCS systems are limited. The first amine scrubbers were designed and implemented in the 1930s [2] and they continue to be the dominant technological solution in commercial CCS systems today. However, despite their long history, amine scrubbers suffer from significant operating energy penalties, footprint challenges and environmental, health, and safety (EHS) concerns. Progress on alternatives is rapidly accelerating, especially with respect to modified amines as well as non-amine solvent systems. However, these systems continue to be relatively complex and CAPEX intensive.



Anyone can design a carbon capture system. It's what you put in it that counts.

Metal-organic frameworks (MOFs) are a class of materials that have shown significant promise in myriad applications for several decades. Their broad industrial adoption has been constrained by a lack of manufacturing scale and exorbitant pricing. Promethean Particles is pioneering a paradigm shift when it comes to the industrial scale manufacturing of cost-effective MOFs.

Since the publication of our first white paper in March 2022, interest in MOF-based CCS systems has accelerated rapidly and been accompanied by significant advancements in the technology. Our customers and other CCS value chain participants

are increasingly drawn to the potential MOFs are showing, especially since they address many of the shortfalls incumbent technologies experience.

MOFs continue to show a lot of potential as adsorbent materials for carbon capture, with certain structures exhibiting two very important properties; preferential ability to adsorb CO₂ over other gas stream species (*selectivity*) and the ability to adsorb significant amount of CO₂ per unit volume of MOF (*uptake capacity*) – the latter typically hitting the headlines. Synthetic chemists in industry and academia will therefore continue to develop new MOF structures with ever-increasing raw CO₂ *uptake* capacities.

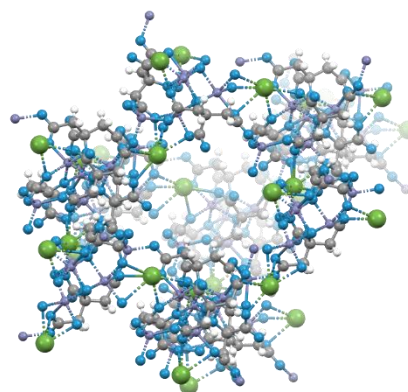


Figure 1: UTSA-16 Crystal Structure - A promising CCS MOF in various forms

Based on our interactions with emitters and engineers in the field of MOF-based CCS systems, we feel broader consideration beyond CO₂ *uptake* needs to be given. We have identified four **thematic pillars** and *eight individual factors* for consideration. We explore each pillar and factor and explain why focusing solely on CO₂ *uptake* can be misleading, potentially resulting in the deselection of perfectly suitable MOF candidates.

Before introducing and discussing each of the eight factors, a brief overview of MOF-based CCS systems and their application is provided for context.

MOF-BASED CARBON CAPTURE AND STORAGE SYSTEMS

DESIGNS FOR MOF-BASED CCS SYSTEMS ARE STILL EMERGING. CURRENT CONSENSUS IS LEANING TOWARDS A MULTI-COLUMN DESIGN; AN ARRAY OF IDENTICAL GAS STREAM CONTACTORS (BEDS) OPERATING IN AN ALTERNATING SEQUENCE THAT ENABLES CONTINUOUS CO₂ CAPTURE.

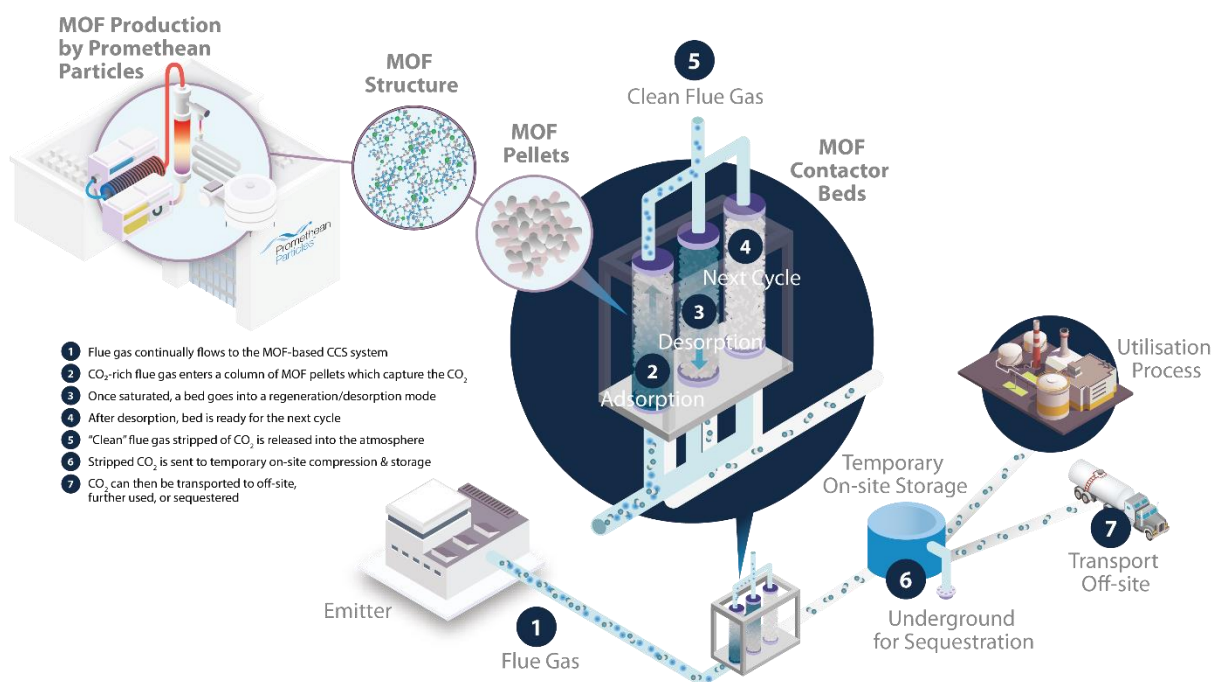


Figure 2: Schematic representation of a MOF-based carbon capture system.

As mentioned in our first white paper, no adsorbent material has infinite capacity and therefore, at some stage, it will be necessary to regenerate saturated material, capture the adsorbed gas, and free up the MOF bed to capture fresh CO₂. The energy used to perform this regeneration is typically the primary cost for any CCS process and so minimising this value is desirable in any system. One advantage of MOFs is that they can trap large amounts of CO₂ via a process called physisorption, whereas incumbent technologies like amines rely solely on chemisorption. In physisorption, van der Waal forces govern the interactions between the adsorbate molecules and adsorbent, whereas chemisorption relies on valence forces [3]. These two processes have vastly different energy profiles. MOFs have been developed with regeneration

energies in the ~30 kJ/mol range, compared to ~70 kJ/mol for amine-based adsorbents [4].

The target CO₂ containing gas stream is flowed through a column containing MOF pellets, granules, or other 'shaped' forms. One advantageous property that certain MOFs exhibit for CCS applications is their *selectivity* for CO₂ over other flue gas components. CO₂ is preferentially adsorbed onto and into the MOF structure whilst other gas species can pass through the column unhindered. The MOF will eventually become saturated with CO₂ and no longer be able to adsorb further CO₂ from the gas stream. How quickly this occurs depends on several factors including the CO₂ *uptake* capacity of the MOF and the flow rate of the incoming gas stream. At or before the point of saturation, the flow of gas is typically diverted to the next available MOF-filled column. The

saturated column is then regenerated to remove the captured CO₂ for subsequent storage, sequestration, or utilisation. Broadly, two strategies can be taken to regenerate saturated MOF materials.

Temperature swing adsorption (TSA) involves initially adsorbing CO₂ at a low temperature ($T_{(Ads)}$) then increasing the temperature of the column to effect desorption ($T_{(Des)}$). The increased temperature shifts the equilibrium towards the gas phase, effecting release of the CO₂. TSA can be particularly advantageous where a significant source of direct or indirect waste heat is available from nearby processes. The main disadvantage of TSA systems relates to the slower adsorption/regeneration cycle times. This is mainly due to the inherent poor thermal conductivity of MOFs, necessitating careful design of the regeneration heat transfer system to effectively heat the MOF to the required desorption temperature. MOFs requiring a lower required regeneration temperature would therefore yield advantages through reductions in the overall energy consumption and the associated reduced time for complete process cycling. This would allow more CO₂ to be captured per unit volume and/or within a given timeframe.

Pressure swing adsorption (PSA) involves adsorbing CO₂ at a relatively high pressure ($P_{(Ads)}$) then reducing the pressure in the column ($P_{(Des)}$) to effect desorption. If $P_{(Des)}$ is below atmospheric pressure, this can be termed vacuum swing adsorption. PSA is typically a faster cycling process than TSA and, at low $P_{(Ads)}$, is more energy efficient.

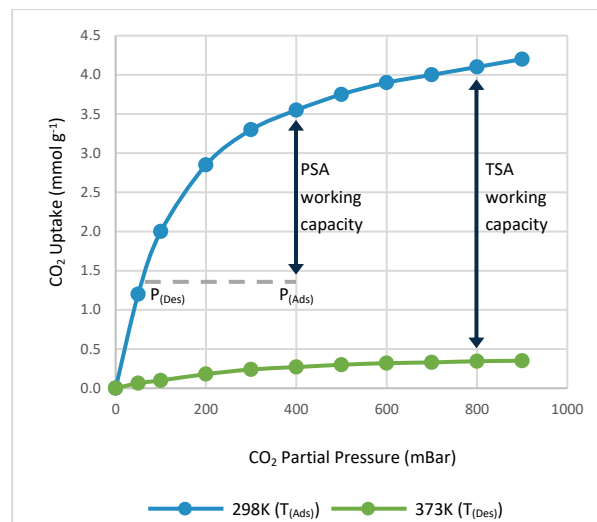


Figure 3. PSA and TSA working capacity for a representative MOF sorbent.

These two strategies can also be combined into temperature and pressure swing adsorption (TPSA) although this approach can add significant complexity to system design.

Applications for MOF-based CCS

CCS processes utilising MOFs are being applied to a range of point source emissions in proof-of-concept designs, including pre- and post-combustion as well as for Direct Air Capture (DAC). The design of the capture system, and the requirements of the MOF used, hinge on the characteristics of the gas stream targeted for CO₂ removal.

The composition of a target gas stream plays a significant role in determining the system design and MOF choice but will vary depending on its source. Post-combustion flue gas streams typically comprise 5-20 vol% CO₂, depending on the fuel used, with the bulk of the remaining gas volume taken up by nitrogen (N₂). Common contaminants in post-combustion streams are oxygen (O₂),



carbon monoxide (CO), sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (VOCs) and water vapour (H₂O). Other point-source examples include gas streams from anaerobic digestion and steam-methane reforming. In these cases, CO₂ concentrations may reach up to 40 vol% and be mixed with gases such as methane (CH₄) or hydrogen (H₂). Meanwhile, DAC, with atmospheric air used as the inlet stream, sees far lower CO₂ levels – ca. 420 ppm (~0.04%). The exact composition of the target capture stream has several implications on MOF selection. Crucially, the *uptake* capacity for a given gas species is dependent on the local partial pressure of that gas around the MOF. A higher concentration of CO₂ in the inlet stream will generally result in higher *uptake* of CO₂. *Selectivity* is also impacted by the gas stream composition. *Selectivity* for a given species tends to increase as its partial pressure increases. Finally, some gas stream components have implications for long-term *stability*.

As well as the available concentration of CO₂ and the types of contaminants present, the flow rate of the incoming stream will inform the MOF choice and system design. Moreover, the availability of waste heat from upstream combustion processes will dictate decisions on whether TSA or PSA is more appropriate for maximising energy efficiency.

As well as benefits in lower energy requirements of adsorbent regeneration, the option for PSA in MOF-based CCS systems offers another advantage over liquid sorbent technologies. Without the need for large reboilers to regenerate the MOFs, the footprint of the CCS system can be a fraction of the incumbent technology. This opens opportunities for carbon capture to be a viable technology at small and medium scale emission sites where space constraints may otherwise have posed challenges.

* Global Carbon Project 2022

** Typical values validated via Breakthrough Analysis

*** Reference point based upon 15-minute cycles over a period of 2 years. Cycling rate is application and system design dependent.

THE ENORMITY OF THE CLIMATE CHANGE CHALLENGE IS HAVING UNPRECEDENTED IMPACTS ON MATERIAL TECHNOLOGIES

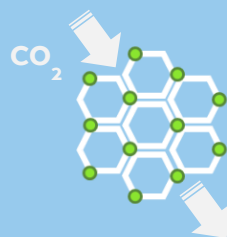
41 Bt 37 Bt



Global anthropogenic CO₂ emissions*



Fossil CO₂ emissions (Power Generation, Industrial Processes, Manufacturing*)



8-10 wt% MOF CO₂ adsorption**



~35,000 cycles/year***

2.3–2.8 Mt
MOF required per year
(for USA and EU27 only)

Whilst we obviously don't expect MOFs to be the only material solution, the volumes required are staggering, especially when you consider that MOFs have historically been discussed in milligram quantities.

FACTORS CONTRIBUTING TO INDUSTRIAL VIABILITY

As MOF-based carbon capture systems continue to advance and gain traction, the potential huge market size for a high performing MOF is driving frenetic academic and industrial research into the development into new MOF structures. This is welcome activity. Out of the approximately 100,000 different MOFs developed since the early 1990s, our experience points to only 10 or so structures that seem to be viable candidates for industrial scale MOF-based carbon capture, when all factors are considered. There is clearly room for improvement in the current stable of MOF candidates for this growing application.



Figure 4. Pillars and Factors to be considered when assessing the industrial viability of a potential CCS MOF.

The chosen MOF within a CCS system is just one component in a complex design. Beyond raw CO₂ uptake performance, there are several other factors that heavily influence system performance, as well as operating and capital costs. Promethean frequently supports such system developers, and increasingly those developing new MOFs. Our goal is to offer insights and guidance around optimal MOF selection and utilisation from a manufacturing perspective. The greatest performing MOF will never be a viable candidate if it can't be manufactured safely, economically and at the scale needed for these applications.

Through these collaborations and our own development work, we have identified eight key factors as important determinants of a MOF's potential industrial viability (see Figure 4). Each factor can largely align to one of four pillars; **Performance, Economics, Supply Chain** and **Environmental, Social, and Governance (ESG)**. Whilst some factors align strongly with just one pillar, many factors span other pillars and impact other factors.

Performance

How a particular MOF performs in each CCS application can be described in several ways. The two most widely reported metrics are CO₂ uptake and selectivity. Whilst these are clearly application performance metrics, they have implications on other pillars and factors. For example, a MOF with higher CO₂ uptake capacity and higher CO₂ selectivity can be more efficient, requiring less volume of sorbent for the same carbon-adsorbing duty – ultimately lowering cost. Similarly, a more stable material potentially needs to be replaced less often, prolonging material life and reducing OPEX costs. If the MOF in question cannot be recycled, a higher stability will lead to less frequent disposal of the MOF, improving its overall ESG profile. These factors are now discussed in more detail.

CO₂ Uptake

There are two key considerations when discussing CO₂ uptake; uptake capacity and uptake rate. The rate of CO₂ uptake into MOFs is typically so fast (the rate at which CO₂ diffused from the surface into the MOF's internal voids) that the gaseous diffusion rate across the entire MOF bed will be the limiting factor. This renders discussion about CO₂ uptake rate as a key consideration essentially moot. Therefore, in the discussion below, all subsequent references to CO₂ uptake are in relation to uptake capacity.

CO₂ uptake capacity refers to the amount of CO₂ a MOF can adsorb or capture at a given pressure and temperature. The higher its CO₂ uptake

capacity, the more CO₂ that can be captured per unit volume of MOF, per capture cycle. Whilst clearly a crucial metric when selecting a MOF candidate for a CCS system, care must be taken to ensure the *uptake capacity* referenced is under conditions relevant to the specific application in question. It is common to report absolute *uptake* capacities at 298 K in 100 kPa of pure CO₂. Whilst this might be a useful standardised approach, this is rarely representative of *uptake* capacities typically exhibited in more real-world conditions, for example at lower CO₂ partial pressures in the range of 5-20 kPa. The shape of a MOF's CO₂ *uptake* isotherm has implications for both *selectivity* and regeneration performance, both of which are discussed in more detail below.

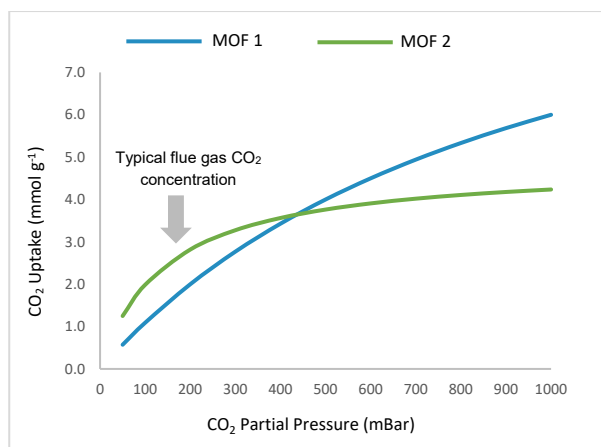


Figure 5. Comparison of CO₂ uptake isotherms for two representative MOFs. At first glance, MOF 1 appears to be superior, exhibiting a higher absolute uptake capacity at atmospheric pressure. However, for a CCS system targeting a gas stream with a CO₂ partial pressure <420 mbar, MOF 2 demonstrates a higher CO₂ uptake capacity so would be the better choice.

Selectivity for CO₂

At its core, CCS is dependent upon a separation technology, so the adsorption *selectivity* of a MOF is arguably more important than its overall CO₂ *uptake* capacity or rate. One of the main advantages of MOFs over other sorbents is their tunability with respect to pore sizes and chemical structure, allowing the targeted adsorption of specific guest species whilst excluding others.

Selectivity is defined as the ratio of two (or more) species adsorbed by a material under a given set of conditions (see Equation 1) and can be predicted

using Ideal Adsorption Solution Theory (IAST) but is notoriously difficult to measure in practice.

$$S_{(Ads)} = \left(\frac{q_1}{q_2}\right) / \left(\frac{p_1}{p_2}\right)$$

Equation 1: Calculation of selectivity, where q_1 and q_2 are the molar loadings (in mmol/g) and p_1 and p_2 are the partial pressures of species 1 and 2 (in mbar).

Using IAST, the pure component isotherms are measured for each gas species, then their *uptake* capacities at the relevant component partial pressure compared. Whilst IAST provides an estimate of the MOF's *selectivity*, it neglects to consider any interaction between adsorbed species. For example, competition and interactions from clustering or pore blockage effects may alter the quantity of each species adsorbed [5]. A representative method of measuring 'real-world' MOF *selectivity* in a laboratory environment, is via dynamic breakthrough analysis (BTA) [6]. The composition of a target gas stream is measured before and after transit through an adsorption column containing the MOF sorbent, thereby giving detailed and valuable information on the relative *uptake* rates of different gas species in combination.

Whilst *selectivity* for CO₂ over bulk components of the gas stream is paramount to achieving efficient separation, *selectivity* for CO₂ over contaminants (such as SO_x, NO_x, VOCs, and water vapour) is also important in CCS systems. Whilst this can often be sidestepped via thoughtful process design (e.g., installing SO_x scrubbers up-stream of the CCS unit) this can add complexity to the overall system design as well as increased CAPEX and OPEX costs.

Stability

When a MOF-based CCS system is operating, the candidate MOF will be subject to many temperature and/or pressure fluctuations during regeneration cycles. The rate at which this cycling will occur will depend on the specific application. A viable MOF must be sufficiently robust, both chemically and mechanically, to maintain acceptable

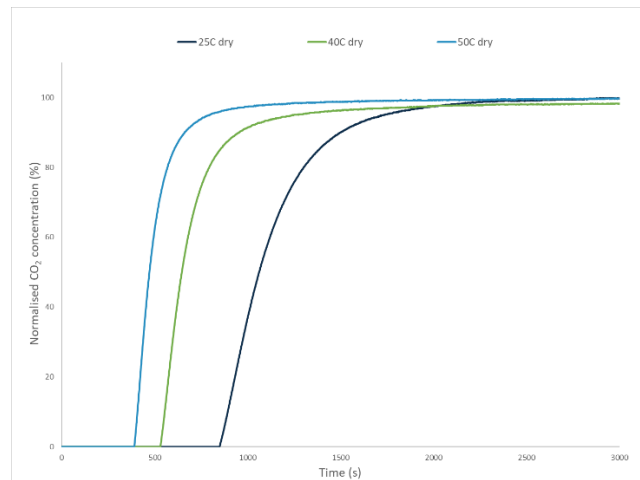


Figure 6: Promethean's new state of the art break-through analyser (BTA) (left) and resultant break-through curves for a representative MOF exposed to simulated flue gas at three different adsorption temperatures (right). These curves show how no CO₂ is being detected downstream of the BTA's MOF bed for different periods of time. The MOF eventually becomes saturated and post-MOF CO₂ "breakthrough" is then detected.

performance after many cycles, typically into the tens of thousands. Not only is this required from a performance standpoint, but also from a cost perspective. Current estimations from a combination our own work and customer discussions, suggest MOF sorbents will require a useful lifetime of 2 to 3 years to be considered economically viable, however this is typically based upon an expected adsorption/desorption cycling rate. Clearly, where MOFs frequently or prematurely degrade, lose performance and/or require replacing with fresh material, the cost of system operation will increase.

The *stability* of a material has an important impact with respect to its *Environmental, Health and Safety (EHS) profile*, particularly its environmental fate. Current liquid amine sorbents are known to degrade during heated regeneration cycles and emit toxic and corrosive degradation products [7]. These spent amines then need to be contained before being safely disposed of in order to minimise pollutive effects. When talking to customers, particularly those who have yet to adopt CCS technology, these concerns are commonly articulated when discussing the use of amine-based systems. They are viewed by some as a reason why CCS technology has yet to be utilised more broadly, despite the fact it is a relatively established technology.

Whilst MOFs are generally more thermally robust than common amine sorbents, a spectrum of

stability effects exists within the MOF class of materials. The aforementioned factor of *selectivity* can play a role in the MOF's performance *stability*. Where a MOF has poor *selectivity*, it can adsorb undesired species that could require higher regeneration energies than the CO₂, and, in some cases, can poison and/or result in the chemical degradation of the MOF. Ultimately, the regeneration conditions required are as, if not more, important than CO₂ capture performance. Factors such as thermal conductivity and heat capacity should be reported more often.

Economics

Carbon capture utilising MOFs is being rapidly developed as a next generation technology, to help overcome some of the performance, energy-efficiency and EHS limitations experienced with existing technological approaches. MOF-based CCS shows a lot of promise from a performance perspective, yet there clearly needs to be an economic viability to the technology. MOFs have historically suffered from perceptions of exorbitant prices. This has led many to question if it is remotely feasible to manufacture and sell these materials at the scale and associated price necessary to make a dent in the ongoing fight against climate change. Manufacturing costs, raw material costs, and raw material abundance all have, and will continue to have, a significant impact on the cost of MOFs. When developing or choosing

a MOF for a CCS application, continued attention to these factors is critical.

Manufacturing Cost

Manufacturing methods that carry significant challenges in upscaling could prove prohibitive to realising the required scale; for example, processes that require additional measures to mitigate health and safety risks, or are unreliable in delivering consistent product quality. MOFs manufactured using such methods will not be viable for industrial application until development work can result in a safe and reliable production route. Meanwhile, MOF manufacturing routes that require significant amounts of energy and/or time, or are labour-intensive, may be feasible to upscale but will inevitably bring with them high production costs. The resulting high price for the MOF may not be viable in the CCS market.

The various processes involved in the synthesis of MOFs can vary depending upon the particular MOF being manufactured and the product form requested by the customer. Accordingly, typical cost parameters – type and source of raw materials, number of process steps, manufacturing equipment, energy and utility requirements, labour costs – can all vary significantly.

There are currently several different approaches to the manufacture of MOFs and not all approaches are suitable for every MOF candidate. The classical method is solvothermal batch synthesis, where all the raw materials are loaded into a vessel and heated to initiate the synthesis reaction(s). This

approach has most likely yielded the majority of the different MOF structures so far reported.

However, batch synthesis is not without its challenges. The need to safely load all materials into a vessel and consistently heat, hold, and cool the reaction mixture provides little processing flexibility. Additionally, batch chemical processing can be much less efficient to scale, and considerably more CAPEX intensive. We contend that the limitations of batch processing are one of the reasons why MOFs have failed to gain the industrial traction that was initially expected for such a promising class of materials with their very valuable performance characteristics.

Promethean's proprietary continuous flow manufacturing process is a considerable advantage in large-scale, low-cost manufacturing of MOFs. In addition to a significant increase in processing flexibility brought about by the ability to independently control flow rate, temperature, and concentration ratio of each reactant, the achievable throughput has a significant input on cost performance. For proprietary/confidential reasons, cost structures are not disclosed here, but we have shown that our continuous manufacturing process helps achieve orders of magnitude lower costs, and essentially renders CAPEX and conversion costs insensitive to the final product cost, a critical consideration when assessing how to efficiently scale into the millions of tonnes. This does place an increased significance and importance of sourcing lower cost raw materials, something discussed below.



Promethean's continuous flow synthesis manufacturing is helping deliver cost effective, industrial scale MOFs for use in carbon capture and other decarbonisation applications.

New IP is extending these capabilities further, helping address unprecedented volume requirements for the fight against climate change.

Raw Material Costs

Typical raw materials for the manufacture of MOFs include a source of the metal ion, usually a metal salt, an organic ligand, and solvent, used either as a carrier fluid and/or heat transfer medium. The raw materials required for synthesising, purifying, and activating MOFs differ between compositions. Some MOFs reported in the literature show excellent performance characteristics but are comprised of niche ligands and/or precious metals [8]. Where the supply of these raw materials is limited or is currently in demand from other high-value industries, they are likely to be expensive to procure. No matter how cost-effective the production process is or becomes, the cost of these raw materials will be a major contributor to the overall cost of the MOF product. Where production processes are both OPEX and CAPEX efficient – for example, Promethean’s continuous flow manufacturing – raw material cost is likely to become the single largest cost component. For large scale applications such as CCS, the market will apply price pressure on the CO₂ adsorbent and any inability to lower cost over the long run will further constrain the adoption of the technology.

Increased attention to current and future raw material prices needs to be given during the material development stages and when choosing a MOF for a particular application. One possible approach to decreasing raw material costs is the full or partial substitution of the metal or ligand. For example, swapping out expensive metal ions or salt sources for more commoditised, cheaper ones can result in a ratio of mixed metals that provides more balanced cost and performance. The substitutions are likely to have some effect on CCS system performance. For example, the substitution of a certain metal or ligand may lead to a drop in CO₂ uptake capacity. However, this doesn’t mean the substitution should be prematurely discounted. If the new metal or ligand was sufficiently more economical, then an increased volume of MOF could be used to make up for the drop in CO₂ uptake capacity—ultimately still delivering the same system performance. Therefore, the overall system should be evaluated using all the factors outlined here which could in fact lead to a more economically viable and sustainable MOF choice.

Supply Chain

The three factors we most closely associate with the **Supply Chain** pillar are *Raw Material Cost*, *EHS Profile* and *Raw Material Availability*. *Raw Material Cost* is described above under the **Economics** pillar and *EHS Profile* is covered in more detail below as part of the **ESG** Pillar. Here we describe the importance of giving due consideration to *Raw Material Availability* when developing and/or selecting MOFs for a CCS application. In this context, we refer to “availability” from two perspectives; natural raw material abundance, particularly as it relates to metals used in the MOF structure, and supply chain availability, i.e., the willingness and ability of manufacturers of MOF precursor chemicals to scale their supply chain to the volumes required.

Raw Material Availability

The extent of global carbon emissions is so significant that the growing adoption of carbon capture technology will require substantial volumes of sorbent materials; this is just as true for MOFs as for other materials. As the manufacture of a target MOF is upscaled, the associated supply chain must be able to scale accordingly. Limitations in raw material availability, coupled with expectations of increased demand, will naturally drive prices higher. Aside from the obvious financial implications, the availability of raw materials will have a significant impact on supply chain stability and security.

Take for instance the ligands used for MOF synthesis. These range from highly specific, niche compounds [9] that are relatively expensive and only available from small, specialised suppliers, through to global commodity chemicals, such as terephthalic acid, fumaric acid, or citric acid [10], that are widely available in large quantities and from multiple sources.

There are reports of MOFs whose structures are based upon exotic ligands. Where these ligands have few wider industrial uses, they are less likely to be economically manufactured in the short-term by multiple suppliers and may not be available beyond the kilogram scale. If demand for MOFs based on these ligands were to increase significantly, many ligand suppliers are likely to

consider upscaling their production. Nevertheless, the fact they may already be considered “exotic” would imply that there is some restriction on availability. This could be that a raw material is in short supply, the process is difficult to scale, or there is intellectual property giving control of the material to a single supplier. Therefore, it is possible, but unlikely, that multiple suppliers will emerge quickly to respond to increased demand. MOF production chains reliant on one supplier would be insecure and unstable. Furthermore, for some other ligands, it is not feasible to reliably, safely, and cost-effectively upscale their required production processes to meet growing demand. With no production supply chain, the MOF in question is simply not industrially viable.

The metal(s) in the MOF, and the supply chain for those metals, also has a substantial bearing on whether a MOF can be a viable candidate for large scale CCS. Certain metallic elements face serious threat over the coming century due to diminishing availability [11], coupled with increasing demand from other applications, including other

technologies addressing a different aspect of the decarbonisation mix, for example electric vehicle batteries and green hydrogen electrolysis. The synthesis of CCS-relevant MOFs using metals in short supply, such as indium, has been described [4]. As well as the high raw material cost, the scarce supply of the metal source makes these MOFs unviable for industrial scale consideration. On the other hand, there is a plentiful supply of metals such as iron, calcium, and magnesium, which are also common in CCS-relevant MOF structures [12]. The abundance of these metals will positively impact the current and future stability of MOF supply chains, and the associated cost of raw materials. The increasing use of advanced materials for alternative decarbonisation technologies will increase the demand for, and use of, certain elements. Overlaps in material demand for these technologies and MOF-based CCS may be inevitable, but avoiding this during early material development and selection could minimise future upscaling challenges.

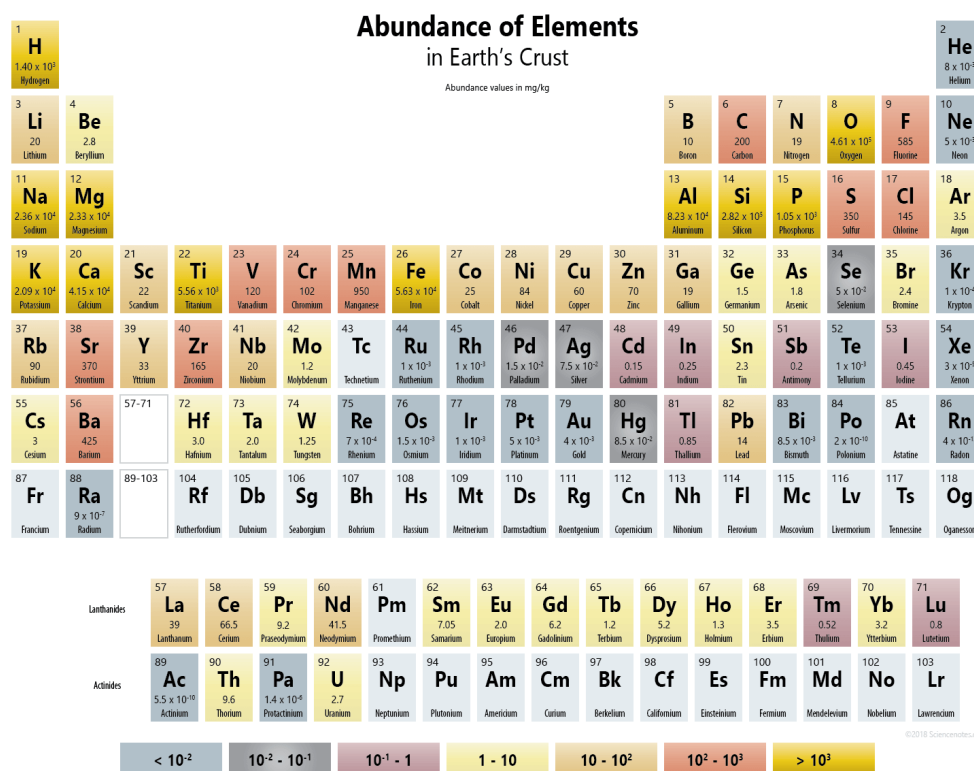


Figure 7: Abundance of elements in the Earth's Crust shown on the periodic table [11]

There is increasing scrutiny on supply chains using tantalum, tungsten, gold, and tin as these are frequently sourced from conflict minerals [13], extracted from areas of political instability, where groups have profited from their mining to propagate violence and war. MOF synthesis for CCS applications using these metals have been described [14] but developing or selecting such MOF products would see significant challenges when it comes to upscaling and building supply chains – from increased societal pressures on ethical trading, to availability of raw materials as suppliers audit their backward supply chains for **ESG** compliance.

Environmental, Social and Governance (ESG)

When first determining the four pillars in our eight factor model, the first iteration had a pillar described as Environmental, Health and Safety (EHS). However, as we continued to explore the important considerations for each factor and their ramifications for various MOF candidates, we felt it prudent to widen this pillar into **Environmental, Social, and Governance (ESG)**. **ESG** as a framework has evolved in recent years from other movements with respect to EHS, pollution reduction and corporate social responsibility. From an industrially viable MOF perspective, initial thoughts were given to those EHS matters, however when it comes to the overlap with supply chain, we feel that **ESG** is a more relevant pillar to accommodate ever-strengthening policy frameworks from companies that will be involved in the life cycle of MOFs when used in CCS applications. Before describing the relevant factors for this pillar, we discuss how we see the MOF sorbent lifecycle developing and why it will be increasingly important to understand its various elements.

Life Cycle of MOF Sorbents

The industrial viability of any new technology is increasingly being determined beyond the traditional assessments of the parameters affecting its use. The entire lifecycle of technologies is now being reviewed more systematically and rigorously,

even giving rise to new ISO standards (14040 and 14044).

This is particularly the case with technologies purporting to have a positive impact on the environment and the climate, so-called “climate-tech.” Potential customers are rightly keen to understand that any technology they are considering doesn’t help address one world problem at the expense of one, or several, others. A good example would be the debate regarding the pros and cons of electric vehicles. Whilst the initial benefits are seemingly obvious – helping eliminate a large source of pollutants, fossil fuel utilisation, and greenhouse gas emissions – that view can change when considered in the light of rare earth metal mining processes and end-of-life battery disposal requirements.

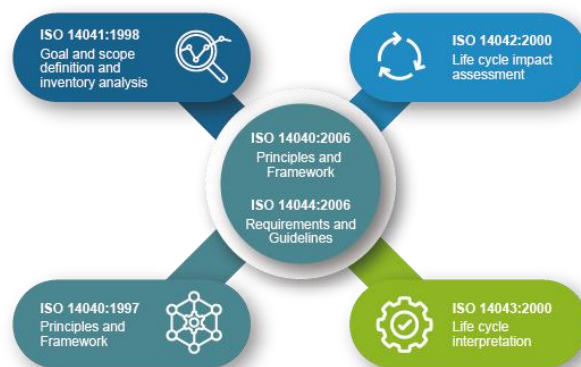


Figure 8: Depiction of how the various ISO life cycle assessment standards interact and combine.

The lifecycle of a material typically encompasses several phases; the raw materials required and the processes used to acquire them combined with the processes used for the material’s manufacture (the production phase), where and how it is distributed and utilised to fulfil its intended purpose (the use phase) and, finally what happens to it once it is no longer useful for its intended purpose (its end-of-life phase).

With respect to MOFs, and particularly Promethean’s proprietary method of manufacturing them, we see end of life *recycling* as a real possibility. Initial experiments have shown very positive results, but much work is required to establish this as a consistent process. In situations where an exhausted/spent MOF can be *recycled* to yield its raw materials once again, the lifecycle is

considered as 'cradle-to-cradle'. Conversely, if recycling is not feasible or viable and the MOF is directed to landfill or other disposal method, the lifecycle follows a 'cradle-to-grave' model.

The eight factors we see as affecting industrial viability can be relevant to one or multiple phases of the MOF's lifecycle. Therefore, identifying the relevant lifecycle processes for each MOF is also vital to help inform its ultimate industrial viability.



Figure 9. The different phases of a MOF during its lifecycle.

EHS Profile

We often hear from customers that one of the reasons driving their interest in MOF-based CCS is that the current stable of amine-based CCS solvents pose several potential challenges. We have first-hand reports of customers stating that they, “don’t want to become a chemical company,” or that they, “don’t have space for carbon capture.” This impression has been formed from their understanding of what it will take to purchase, utilise, and dispose of amine-based solvent sorbents and their end-of-life by-products. It’s certainly evident that end-users, and potential end-users, of CCS systems require a better awareness and understanding that alternative technologies exist and are being actively developed.

MOFs, as a class of materials, broadly offer potential as CCS sorbents with a preferable *EHS profile*. As stable solid sorbents, MOFs offer a variety of advantages in transportation, handling, and use. There is little risk of spillage/leakage during transportation and storage, or contamination of flue gas. When loaded into CCS

systems, MOFs don’t exhibit some of the same corrosive properties reported when utilising amine sorbents [15].

From a manufacturing perspective, the majority of MOF syntheses described are via wet chemical processes. Promethean has developed considerable expertise optimising the manufacture of MOFs in safer ways, for example by utilising more water-based synthesis methods [16], as opposed to historic solvent-based processes using organic solvents; from alcohols [10] to toxic materials like dimethylformamide (DMF) [17].

The chemical industry has made huge improvements with respect to managing the risks associated with hazardous chemicals and/or processes and some part of the chemical industry is involved in the manufacture of such materials every day around the world. Therefore, a MOF that requires a hazardous chemical as a raw material, processing aid, or includes a higher risk profile manufacturing step is not necessarily unviable. However, our view is that where possible, substitutions should be made for alternative materials and MOFs developed and/or selected for CCS applications with the highest inherent safety profile available.

A current challenge in evaluating the true EHS profile of MOFs is the lack of available safety data due to the relative novelty of MOFs being utilised in any significant quantities. MOFs are currently rightly conservatively regarded with the same safety profile as their raw materials, assuming a safety designation based on the most hazardous. Some initial work suggests this approach is beyond conservative. However, it is clear that conducting the relevant tests and gathering the required information to generate more accurate and relevant material safety data sheets (MSDS) is in the collective interest of advancing the technology. By working together collaboratively, there is the opportunity to advance this practice and speed up the time to market.

Recyclability

As described above, MOFs, like other CCS sorbent materials essentially act as a consumable in the CCS process. They exist to adsorb CO₂ for a targeted period of time. After many cycles, the CO₂ binding sites of the MOF could become blocked,

deteriorating its *uptake* performance to a point where a standard regeneration cycle is no longer sufficient to evacuate the pores. This would determine the need for MOF replacement. Customers have communicated that MOFs should have a minimum useful lifetime of 2 to 3 years when being utilised in CCS systems, but this is heavily dependent upon the cycle rate – in fact, a required number of cycles is actually a more realistic durability/longevity target than time. As a MOF manufacturer and optimiser, Promethean is obviously trying to push this workable lifetime as far as possible, but there is still the expectation that a MOF’s usable life is finite.

At the enormous volumes required to effect meaningful climate change mitigation, an obvious concern becomes end-of-life disposal. Many materials today, including chemicals, are sent for disposal. Depending upon their safety profile, this could be anything from landfill, to incineration, or in the extreme case of nuclear waste, vitrification, and deep-sea storage. Several of the driving goals for MOF-based CCS are to bring about a more planet-friendly CCS solution. We have described how MOF-based carbon capture is significantly more energy-efficient than some alternative technologies, and how the correctly selected MOF has a preferable *EHS profile* than many of the amine-based solvents on the market today. Therefore, we want to ensure that MOFs remain advantageous throughout their entire lifecycle.

There are questions surrounding the realistic and practical end-of-life options for the MOF, whether it can be re-used for another purpose in its used form; if it is destined for landfill; of if it can be broken down to its constituent metal and ligand components and re-synthesised to pristine MOF. There is substantial evidence to suggest that the latter is achievable for some MOF species [18].

We have started our own work in this regard. As a result of the combination of Promethean’s wet flow manufacturing method and our extensive knowledge of MOF synthesis processes, we formed early hypotheses that we should be able to take spent MOF and reconstitute it into functional recycled material. The early work is very promising, and we have successfully demonstrated that recycled MOF is not only possible, but also

performs to expectations in lab-scale CCS applications.

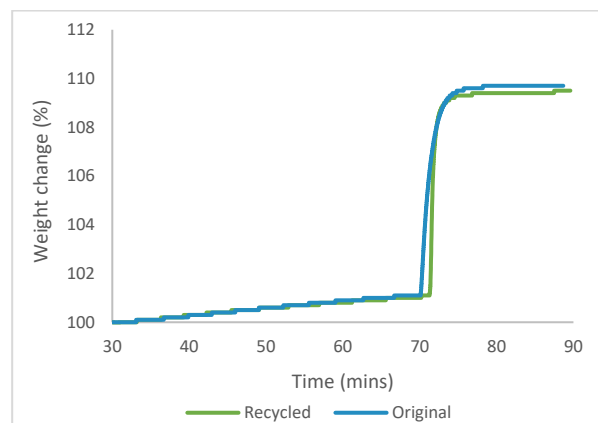
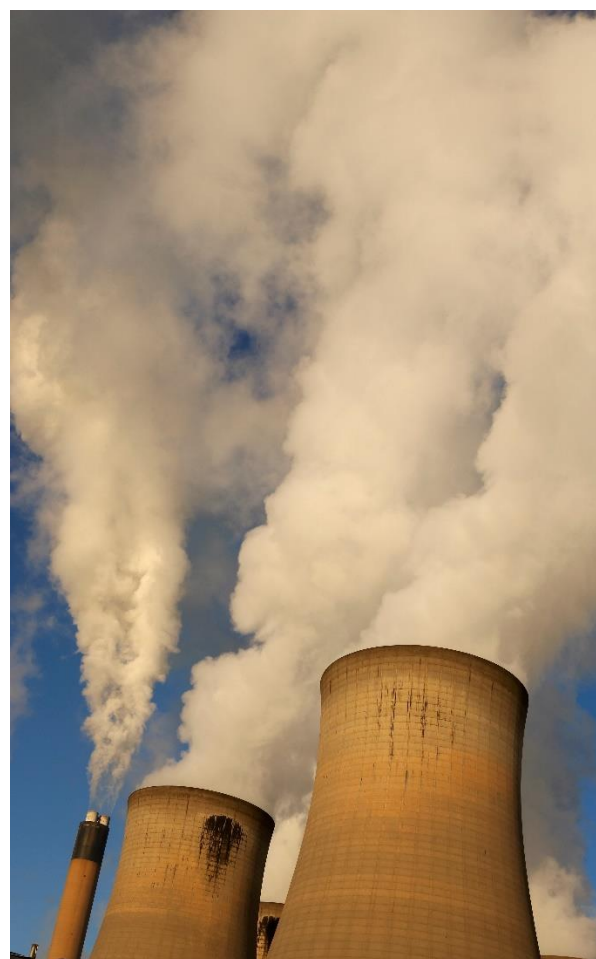


Figure 10: Thermogravimetric Analysis (TGA) curves showing CO₂ uptake for fresh MOFs and a comparison to MOFs that have been recycled and remade using Promethean’s proprietary manufacturing process



CONCLUSIONS

As metal-organic frameworks traverse the bridge between academia and industrial application, there is a need to broaden the scope of considerations beyond CO₂ *uptake*. It is crucial that sorbents are evaluated from the perspective of the system developer, who inherently takes a more pragmatic and holistic view of viability at industrial scale [19].

Through our work, and that of others, the prospect of MOFs for CCS is now real, yet CO₂ *uptake* records continue to grab the headlines. Whilst this may help with publishing papers, attracting funding, and gaining academic accolades, our thesis is a simple one – even the highest performing MOF from a CO₂ *uptake* perspective may not be industrially viable, if:

- It's not sufficiently *selective* for CO₂
- It's not stable and durable enough to last
- We can't source enough of the raw materials
- The raw materials are too expensive
- Complex manufacturing steps are required that reduce capacity and excessively increase cost
- It presents manufacturing and/or EHS risks that can't be mitigated

With the breadth of CCS applications, and the variability in gas streams, a single MOF composition will not be the optimal candidate for

every scenario. Choosing the most viable MOF will require a balance of the different factors discussed in this white paper. The weighting or significance of each factor is likely to vary between applications. Ultimately, it is likely that trade-offs need to be made to yield MOF candidates viable for commercial deployment at the scale required to tackle our global carbon removal challenges.

MOFs represent an exciting new frontier of materials chemistry that have shown initial promise in their ability to selectively capture carbon from a gas stream and then efficiently desorb that carbon. However, to this point, they have suffered from a perception of prohibitive costs and a lack of industrial scale.

At Promethean, our goal is to help those developing MOFs solve one of the world's pressing issues – climate change. Promethean's manufacturing technology is addressing the historical challenges to commercial deployment, by pioneering a paradigm shift in production scale and cost-effectiveness.

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REFERENCES

- [1] P. R. Shukla, J. Skea, R. Slade, A. Al Khourdajie, R. van Diemen, D. McCollum, M. Pathak, S. Some, P. Vyas, R. Fradera, M. Belkacemi, A. Hasija, G. Lisboa, S. Luz and J. Malley, "Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change," Cambridge University Press, UK and New York, 2022.
- [2] G. T. Rochelle, "Amine Scrubbing for CO₂ Capture," *Science*, vol. 325, no. 5948, pp. 1652-1654, 2009.
- [3] O. D. Agboola and N. U. Benson, "Physisorption and Chemisorption Mechanisms Influencing Micro (Nano) Plastics-Organic Chemical Contaminants Interactions: A Review," *Frontiers in Environmental Science*, vol. 9, 2021.
- [4] A. Masala, J. G. Vitillo, G. Mondino, C. A. Grande, R. Blom, M. Manzoli, M. Marshall and S. Bordiga, "CO₂ Capture in Dry and Wet Conditions in UTSA-16 Metal-Organic Framework," *ACS Applied Materials and Interfaces*, vol. 9, pp. 455-463, 2017.
- [5] R. Krishna and J. M. van Baten, "How Reliable Is the Ideal Adsorbed Solution Theory for the Estimation of Mixture Separation Selectivities in Microporous Crystalline Adsorbents?," *ACS Omega*, vol. 6, no. 23, pp. 15499-15513, 2021.
- [6] R. Krishna and J. R. Long, "Screening Metal-Organic Frameworks by Analysis of Transient Breakthrough of Gas Mixtures in a Fixed Bed Adsorber," *J. Phys. Chem. C*, vol. 115, no. 26, pp. 12941-12950, 2011.
- [7] F. Vega, A. Sanna, B. Navarrete, M. Maroto-Valer and V. J. Cortés, "Degradation of amine-based solvents in CO₂ capture process by chemical absorption," *Greenhouse Gases Science and Technology*, vol. 4, no. 6, pp. 707-733, 2014.
- [8] S.-T. Zheng, J. T. Bu, Y. Li, T. Wu, F. Zuo, P. Feng and X. Bu, "Pore Space Partition and Charge Separation in Cage-within-Cage Indium-Organic Frameworks with High CO₂ Uptake," *J. Am. Chem. Soc.*, vol. 132, no. 48, pp. 17062-17064, 2010.
- [9] X.-J. Kong, T. He, Y.-Z. Zhang, X.-Q. Wu, S.-N. Wang, M.-M. Xu, G.-R. Si and J.-R. Li, "Constructing new metal-organic frameworks with complicated ligands from "One-Pot" in situ reactions," *Chem. Sci.*, vol. 10, pp. 3949-3955, 2019.
- [10] Y. Chen, X. Mu, E. Lester and T. Wu, "High efficiency synthesis of HKUST-1 under mild conditions with high BET surface area and CO₂ uptake capacity," *Progress in Natural Science: Materials International*, vol. 28, no. 5, pp. 584-589, 2018.
- [11] T. Helmenstine, "Abundance of Elements In Earth's Crust - Periodic Table and List," 23 May 2018. [Online]. Available: <https://sciencenotes.org/abundance-of-elements-in-earths-crust-periodic-table-and-list>.
- [12] D. Britt, H. Furukawa, B. Wang, T. G. Glover and O. M. Yaghi, "Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites," *Proc Natl Acad Sci USA*, vol. 106, no. 49, pp. 20637-40, 2009.
- [13] European Commission, "Conflict Minerals Regulation," [Online]. Available: https://policy.trade.ec.europa.eu/development-and-sustainability/conflict-minerals-regulation_en. [Accessed March 2023].
- [14] G. Sargazi, D. Afzali, A. Mostafavi and S. Y. Ebrahimpour, "Ultrasound-assisted facile synthesis of a new tantalum(V) metal-organic framework nanostructure: Design, characterization, systematic study, and CO₂ adsorption performance," *Journal of Solid State Chemistry*, vol. 250, pp. 32-48, 2017.
- [15] A. Krzemien, A. Wieckol-Ryk, A. Smolinski, A. Koterias and L. Wieclaw-Solny, "Assessing the risk of corrosion in amine-based CO₂ capture process," *Journal of Loss Prevention in the Process Industries*, vol. 43, pp. 189-197, 2016.
- [16] A. S. Munn, P. W. Dunne, S. V. Y. Tang and E. H. Lester, "Large-scale continuous hydrothermal production and activation of ZIF-8," *Chemical Communications*, vol. 51, no. 64, pp. 12811-12814, 2015.
- [17] F. Debatin, A. Thomas, A. Kelling, N. Hedin, Z. Bacsik, I. Senkovska, S. Kaskel, M. Junginger, H. Müller, U. Schilde, C. Jäger, A. Friedrich and H.-J. Holdt, "In situ synthesis of an imidazolate-4-amide-5-imidate ligand and formation of a microporous zinc-organic framework with H₂- and CO₂-storage ability," *Angew Chem Int Ed Engl.*, vol. 49, no. 7, pp. 1258-1262, 2010.
- [18] X. Sun, H. Li, Y. Li, F. Xu, J. Xiao, Q. Xia, Y. Li and Z. Li, "A novel mechanochemical method for reconstructing the moisture-degraded HKUST-1," *Chemical Communications*, no. 54, pp. 10835-10838, 2015.
- [19] A. K. Rajagopalan, A. M. Avila and A. Rajendran, "Do adsorbent screening metrics predict process performance? A process optimisation based study for post-combustion capture of CO₂," *International Journal of Greenhouse Gas Control*, vol. 46, pp. 76-85, 2016.
- [20] R. D'Amato, A. Donnadio, M. Carta, C. Sangregorio, D. Tiana, R. Vivani, M. Taddei and F. Costantino, "Water-based Synthesis and Enhanced CO₂ Capture Performance of Perfluorinated Cerium-Based Metal-Organic Frameworks with UiO-66 and Mil-140 Topology," *ACS Sustainable Chemistry & Engineering*, vol. 7, no. 1, 2018.