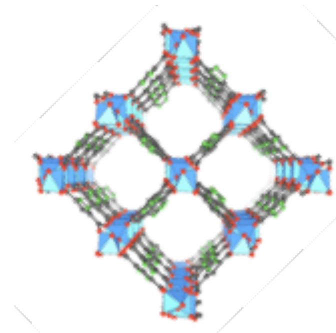
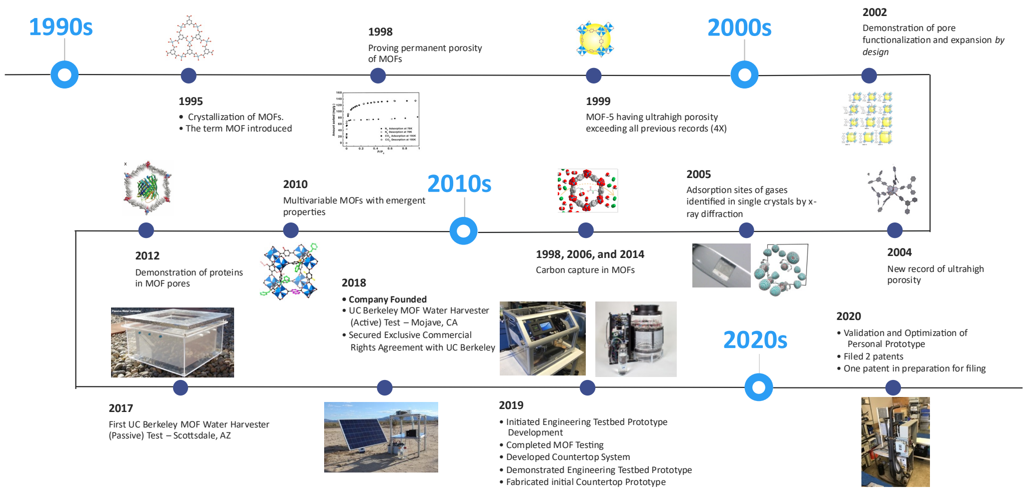
Metal-Organic Frameworks Overview



The centerpiece of Water Harvesting's (WaHa) innovation is the development of Metal-Organic Frameworks (MOFs) to capture water vapor from the atmosphere. The study of MOFs, an area rife with innovation, falls under the discipline of Reticular Chemistry and is focused on linking molecular building units with strong bonds to make dimensional crystalline structures. MOFs are porous crystalline materials constructed with metal ions and linked into rigid three-dimensional (3D) nano-porous structures. These microscopic, three-dimensional lattice-like structures have pores capable of collecting and holding molecules internally and are engineered to capture specific molecules.

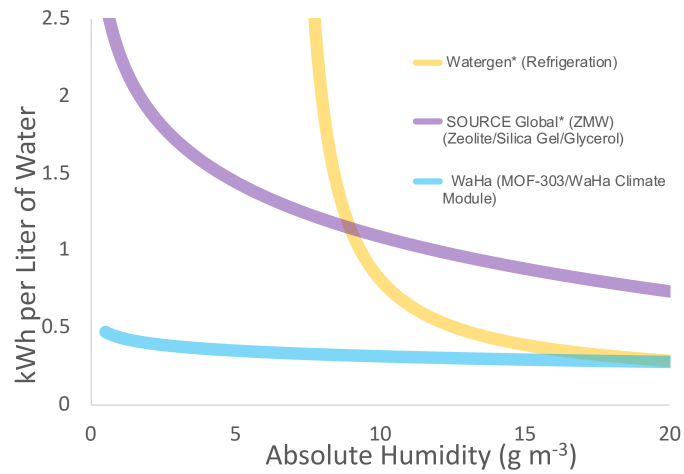
Over the last 25 years more than ninety thousand MOFs have been studied. Numerous applications in many fields are being developed utilizing MOFs including: hydrogen storage, nuclear waste collection, drug delivery systems, and carbon capture.

Evolution of MOFs and WaHa

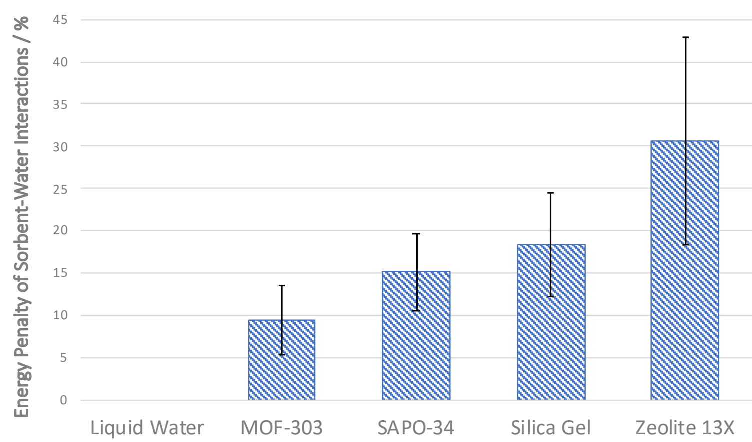


Initially developed at UC Berkeley, Water Harvesting's patented MOF technology is purpose-built to harvest water vapor from the atmosphere. Similar to the way a sponge absorbs water, these nanoporous structures attract and hold only H_2O molecules. Unlike a sponge, the stored molecules have to be mildly heated in order to be released. Upon saturation, our MOF is 40% of its body weight in water. For example, one teaspoon (4 grams) of MOF captures almost 2 grams of water. WaHa MOF structures are both efficient and resilient. In tests of more than sixty thousand cycles, the MOFs show no structural degradation. The MOF is completely recyclable! At the end of the MOFs life cycle, it can be dissolved and reassembled into new MOF structures.

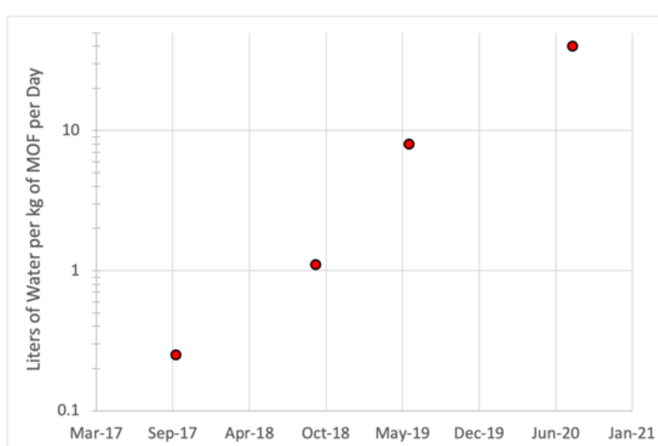
WaHa's MOF technology is revolutionary for Atmospheric Water Generation. It can produce pure drinking water at lower energy costs and with lower absolute humidity requirements than existing AWG systems.



Energy efficiency is sorbent dependent. The following equation models this: $\boldsymbol{Q_{st} = h_{fg} + A}$ Where Q_{st} is the heat of adsorption, h_{fg} is the latent heat of vaporization of liquid water and A is the cumulative energy of sorbent-water interactions. The lower the A value, the lower the energy of adsorption which in turn drives the energy-efficiency of water generating systems. The lower the value of energy adsorption the lower the required temperature of desorption, which in turn determines the coefficient of the performance of water generating systems. MOF-303 provides WaHa with the highest coefficient of performance. Early systems will achieve an energy efficiency of 0.4-0.5 kWh/L while future systems should be able to achieve 0.2-0.3 kWh/L.



The first test of water production capacity was done in the desert in a completely passive (no electrical power) test environment by Professor Omar M. Yaghi (and Eugene Kapustin). Subsequently, testing has been done using an active system, followed by two different test platforms at WaHa. Water production efficiency has improved dramatically with each system.



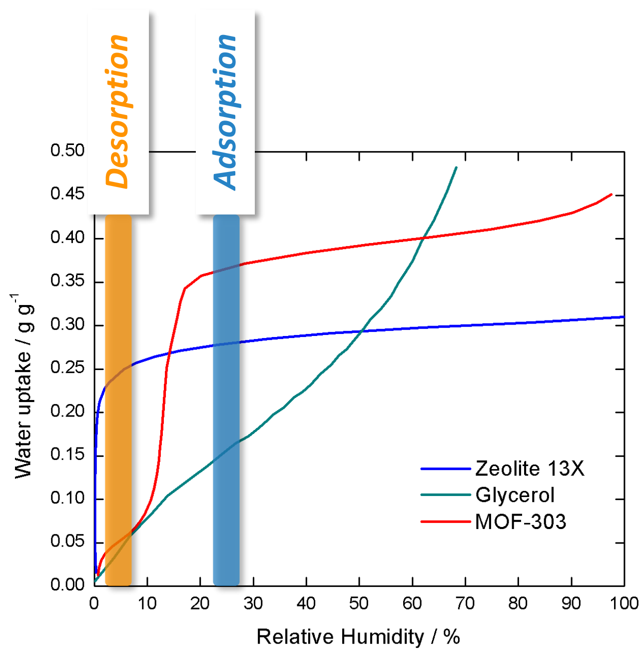
FAQs

Why is this MOF different than other MOFs?

The MOF is constructed on the molecular level from metal-oxide units covalently connected by “organic linkers”, each designed to fit together similar to the way an iron and steel skeleton of a multi-storied building is constructed. This construction results in an infinite arrangement of hollow frameworks that encompass space. It is the space within the structure where molecules of any gas can be adsorbed.

There are several properties of WaHa MOF-303 which make it uniquely well suited for efficient and effective atmospheric water capture.

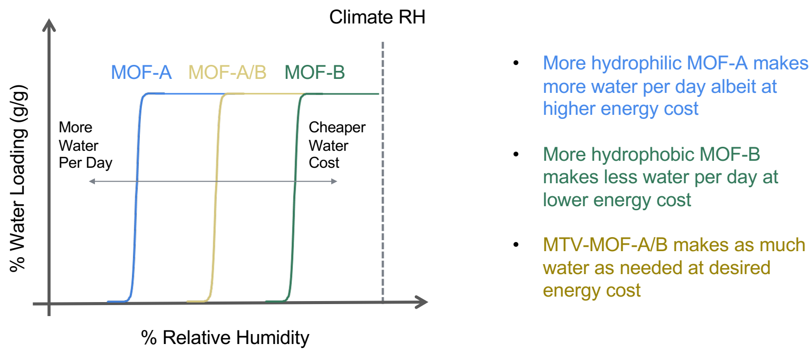
- The pores have specific adsorptive sites that water can freely bind to or reside via hydrogen bonding. These sites are hydrophilic (water “loving”) and therefore can attract water from air with low humidity where the water concentration is preciously low. Because the bonding between water molecules is rather electrostatic and not covalent it takes low-grade heat to break the bond, rendering the desorption process energy efficient.
- It is composed of hydrophilic (metal-oxide units) and hydrophobic (segments of the organic linkers) making its vast pore system ideally suited for accumulating water through the cooperative mechanism without holding onto water too tightly. This allows for a relatively low temperature requirement to remove the H_2O molecule from the pores for harvesting. In other words, the energy of the adsorption of water molecules is lower than in other materials, thus it takes less energy to release water out of the MOF.



- Cooperative mechanisms result in rapid filling of the MOF pore with water which translates into the sharp step in the water isotherm, which is beneficial – MOF is only required to be heated by 20-30 °C to initiate desorption.
- It can adsorb up to 40 percent of its weight in water and the rate of adsorption/desorption is very high. Combined it allows harvesting and delivery of more water per amount of sorbent than any other material.

Is Water Harvesting based around a single MOF?

In addition to licensing MOF-303, WaHa has also licensed the IP filing from UC, Berkeley which describes a "MTV-MOF" strategy (MTV stands for multivariational). This strategy enables construction of MOF structures which can have different organic linkers in them. By mixing hydrophobic and hydrophilic organic linkers with different ratios one can purposely design a MTV-MOF which can capture water in different climates. The MTV-MOF structure which has more hydrophobic linkers than hydrophilic linkers would capture water at more humid climates and vice versa. The isotherm step can be gradually shifted according to the ratio of these linkers in the MOF.



The advantage of using MTV-MOFs based on MOF-303 structure is two-fold:

1. WaHa can design a specific MTV-MOF which would fit any climate in the world – hydrophilic MTV-MOF for arid climates of American Southwest and Saudi Arabia or hydrophobic MTV-MOF for more humid climates of Northern India and Turkey.
2. WaHa can choose which MTV-MOF to use in our water harvester depending on whether one would like to produce more water per day with more hydrophilic MTV-MOF or to produce water at cheaper cost with more hydrophobic MTV-MOF.

How many cycles of adsorption and desorption will MOF-303 maintain its performance?

WaHa has tested MOF-303 for 60,000 cycles with no degradation in performance. We are continuing to test, but we believe there will be no degradation until at least 100,000 cycles.

What are some examples of MOFs that have been commercially successful?

- There are several examples of successful MOF implementation in other fields:
  - NuMat makes MOF to store arsine gas for semiconductor industry and to purify gases avoiding expensive cryogenic separation.
  - BASF/Mercedes vehicles powered by natural gas stored in MOF tanks (presumably, MOF-177)
  - MOF Technologies/Decco manufacture MOF which can store and slowly release 1-methylcyclopropene to control fruit ripening (Note: Decco lost a patent lawsuit in late 2019 and was forced to pull the product)
  - Matrix Sensors make MOF-based CO_2-sensors.

- Large MOF manufacturers such as BASF produce MOF in large quantities already. MOFs can now be purchased even from the Sigma-Aldrich website which are sold under the Basolite name.

Why will MOF-303 be commercially successful for AWG when others haven't been?

MOF-303 will be commercially successful in the field of water harvesting due to its properties described below:

How is MOF-303 different from other desiccants?

When it comes to MOF-303 and water harvesting, our MOF does what other material cannot do. A viable material for water harvesting needs to possess three requirements:

- High water capacity
- Facile kinetics
- Works at low absolute humidity (below 30% RH or 7 grams/m^3)

Zeolites work at low humidity but don't have high capacity. Zeolites require a lot of energy to release water and show a slow desorption rate. Porous carbon has high water capacity but does not operate at low humidity. MOF-303 is the only material which has all three features. In addition, MOF-303 is composed of aluminum metal and pyrazolate-based dicarboxylic acid: which are cheap, benign, and non-toxic compounds. Our chemistry allows for precise control of the particle size which eliminates the risk of nanoparticle pollution. Our synthesis is done in water; the only side product of the MOF synthesis is literally saltwater. Finally, at the end of life for the MOF, the used MOF material can be dissolved in mild base and the aluminum and organic linker material can be mostly recovered to reassemble the MOF again. Almost complete recyclability with a non-toxic process!

Material/ Technology	High Capacity	Fast Kinetics	Low Humidity
Cooling Condensing	NA	NA	✗
Zeolites	✗	✗	✓
Polymers, Hydrogels & Molecules	✓	✗, ✓	✗
Salts	✗	NA	✓
MOF-303	✓	✓	✓

What's the difference in quality of water from other AWG systems?

Our MOF-303-based water harvesting systems produce pure water because MOF-303 works as a nano-separator to exclusively separate H_2O molecules from all other gases in the atmosphere.

There are two reasons why MOF works as a nano-separator of water molecules:

1. Pore size. The diameter of the pore channels in the MOF is 6-7 angstroms or 0.6-0.7 nanometers. Large molecules of volatile organic compounds simply won't fit into the pore due to their bulkiness. This is called "size exclusion" phenomenon. For example, benzo(a)pyrene, a very well-known carcinogen, is about 10 angstroms long and can't diffuse into the MOF pore.
2. Smaller molecules such as carbon dioxide, NOx, SOx, methane, ammonia, hydrogen sulfide potentially can be adsorbed by MOF, however, water molecules will displace them because water provides stronger bonding with adsorption sites in the pore (in particular, hydroxyl groups on the aluminum-oxide chains). This is called "selectivity" phenomenon. Upon completion of the adsorption stage, only molecules of water occupy the pore volume and only molecules of water will be desorbed within the WaHa Climate Module™.

Zero Mass Water. Uses either a zeolite, silica gel, or glycerol as a desiccant. Their system specifications show that a filter is required for water purity.
Drupps. Uses brine, a common liquid desiccant that doesn't possess "size exclusion" effect and absorbs a lot of pollutants from air.
Other dry desiccants: Some other solid adsorbents such as porous carbon and clay may possess size exclusion properties, but they are not selective to water.
Watergen (and all other refrigeration-based systems). These systems capture all pollutants in the water vapor and must be filtered out.

Can you provide some background on MOF, COF, ZIF and any other relevant technologies in reticular chemistry and explain why MOF-303 is the superior material?

Reticular chemistry developed over 20 years ago by Prof. Omar M. Yaghi is the chemistry of linking building blocks by strong bonds to make extended crystalline structures such as MOFs, COFs, ZIFs etc. These materials are primarily used for gas storage (hydrogen, natural gas) and gas separation (ethane/ethylene, xylene isomers), although there are other numerous applications. While we can't state that MOFs in general are better for water harvesting than COFs or ZIFs, MOF-303 is better than any other MOF, COF, or ZIF due to the unique properties of this MOF as outlined above.

What are your plans to reduce the cost of the linker for MOF-303?

We are developing a new way of synthesizing the organic linker via catalytic oxidation with quantitative yield. This method was previously shown to be successfully implemented in synthesis of other simple aromatic dicarboxylic acids on large scale. We are also working on similar linkers which are much simpler to make but result in similar performance.

How many researchers are doing water-based MOF research?

- Over 25 research labs.

Are you aware of any commercial ventures doing water-based MOF product development? If so, how does their technical approach compare to Water Harvesting?

- There is one other company that claims to use a MOF, Molecule (www.molecule.us), but their target market is very small and unlike WaHa, they do not have a standalone product (they cannot generate water with only energy and atmospheric water vapor). Their input is hot, humid air that is a waste product of (usually commercial) dehumidifiers. These are not common products and, in the US, typically only exist in S. California and the Southeast.
    - The water-harvesting material used by Molecule is called ROS-37 designed by Prof. Zaworotko, Bernal Chair of Crystal Engineering, the University of Limerick. Reading the patent, it is made of copper and two organic linkers. It has much lower water capacity in comparison to MOF-303 (just ~8 wt% for ROS-37 to ~40% for MOF-303). But more importantly, one of the graphs in the patent shows a steady decrease in water uptake - after just 19 cycles it loses ~ 10 % of its initial capacity. This is likely due to decomposition of the material. Note: Water Harvesting's CTO, Eugene Kapustin, tried to synthesize this MOF and then coat a mesh substrate, but the coating appeared to be pretty bad. The MOF layer delaminated quickly after the first desorption cycle.
    - In the January 2020 DARPA Lightning talk, Prof. Zaworotko claimed that ROS-37 outperforms MOF-303 and all other known MOFs in terms of adsorption/desorption kinetics time. From what they published in their patent, there is no evidence of that - in fact, it looks much slower. Note: the only MOF selected by DARPA for a large-scale AWG system implementation was MOF-303.
    - The ROS-37 MOF was originally discovered in 2003. It took more than 15 years before the patent was filed.