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USE OF CFD MODELING TO OPTIMIZE CAPITAL AND OPERATIONAL COSTS OF MOLECULAR SIEVE UNITS

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ABSTRACT

A major challenge for industrial operators and EPC firms is to optimize capital and operational costs of both new and existing facilities. Computational Fluid Dynamics (CFD), even though a powerful and comprehensive modeling tool, is not widely used in the molecular sieve industry. This paper will focus on CFD models developed by CECA (Arkema) and their applications to optimize the adsorption and regeneration phases. The first part will discuss ways to optimize the molecular sieve bed designs through insights on bed configuration, hydrodynamics and other process parameters. The second part will address the troubleshooting issues, optimizing and adapting the plant operation under different constraints. The two parts, that are key to cost savings, will be illustrated using real industrial cases.

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1. INTRODUCTION

Molecular sieve beds for dehydration and purification are an integrated part of most of the Gas Plants, Petrochemical Complexes and Refineries. A major challenge for industrial operators and EPC firms in current global Oil and Gas context is to optimize capital and operational costs of both new and existing facilities. This is the reason why it has become paramount for molecular sieve suppliers to bring forward innovative solutions covering products, processes and services to help achieve this challenge.

Industrial adsorption has been the center of intensive research both in academic as well as industrial world. Modeling plays a vital role amongst the numerous tools used to ensure the design and operation of such processes. Over years of research, molecular sieve suppliers like CECA have developed several mature and robust models based on theoretical, experimental and industrial experiences that incorporate the main factors driving the dynamics of the adsorption processes. Nevertheless, these models are often empirical and one-dimensional which limit a better understanding of hydrodynamics. Computational Fluid Dynamics (CFD) is considered as one of the most powerful and comprehensive modeling tool. However, until now, molecular sieve industry did not widely make use of CFD as a tool to examine a problem qualitatively as well as quantitatively. This paper will focus on the CFD model developed by CECA (Arkema) and its application to investigate and optimize the adsorption and regeneration phases.

Adsorption on molecular sieves, though easy to understand, is a complex phenomenon and often provides challenges while designing and operating due to a number of parameters that governs the efficiency of such processes^[1]. A good design accounts for process parameters (flow, temperature, pressure, impurities concentration, etc.) and vessel configuration (type of molecular sieve, split beds, distributor design, grid design, etc.) but also contaminants (olefins, liquid carry-over, hydrocarbon condensation, oxygen, amines, salts, acids, bases, etc.) and other operational challenges^[2,3,4,5] (grid leakage, hydrothermal damaging, channeling issues, insufficient regeneration, etc.). Any of these parameters not considered during design of the unit or changed from the design basis can severely affect the performance of the molecular sieve, thereby, increasing capex (unit design, lifetime) or opex (energy consumption, frequent changeouts, maintenance, etc.). Even though empirical models can evaluate the impact of some parameters, often such models do not accurately predict the impact of a number of parameters that requires better understanding of hydrodynamics. CFD models, therefore, become mandatory in order to help accurately analyze such parameters.

The first part of this article will discuss ways to optimize the molecular sieve bed designs through insights on bed configuration, hydrodynamics and other process parameters. The second part will address the issues that concern troubleshooting, optimizing and adapting the plant operation under different constraints. The two parts that are key to cost savings will be illustrated using real industrial cases and CFD models analysis.

2. DEVELOPMENT OF CFD MODEL

A robust modelling framework within an open source CFD platform using Open FOAM software^[6,7,8] was developed. The model was based on the work of *M. Gholami et al.*^[9,10]. A similar approach was followed for model development, i.e.,

- the adsorbent was taken bi-disperse type^[11]
- the intra-particle mass and heat transfer were represented by Linear Driving Force model^[9,10]
- the adsorption was assumed to take place at the intra-particle micro space throughout a simplified micro-porous diffusion mechanism (no concentration dependency)^[14]
- the mass transfer between inter-particle space and intra-particle macro space was assumed to take place throughout a parallel association of convective and diffusive mechanisms^[11,13]

- the hydrodynamics in the porous media was governed by Brinkman-Forchheimer model
- the flow was assumed incompressible
- a two-fields temperature model was assumed (no local thermal equilibrium)
- in the non-porous volumes, the flow field was simulated using the RANS k- ϵ turbulence model

The model parameters were adjusted with more accurate adsorbent properties, isotherms and other data. For instance, a hybrid dual site Langmuir/Freundlich^[10,12] adsorption isotherm was used to accurately fit the adsorbent isotherms in all pressure and temperature ranges (Figure 1).

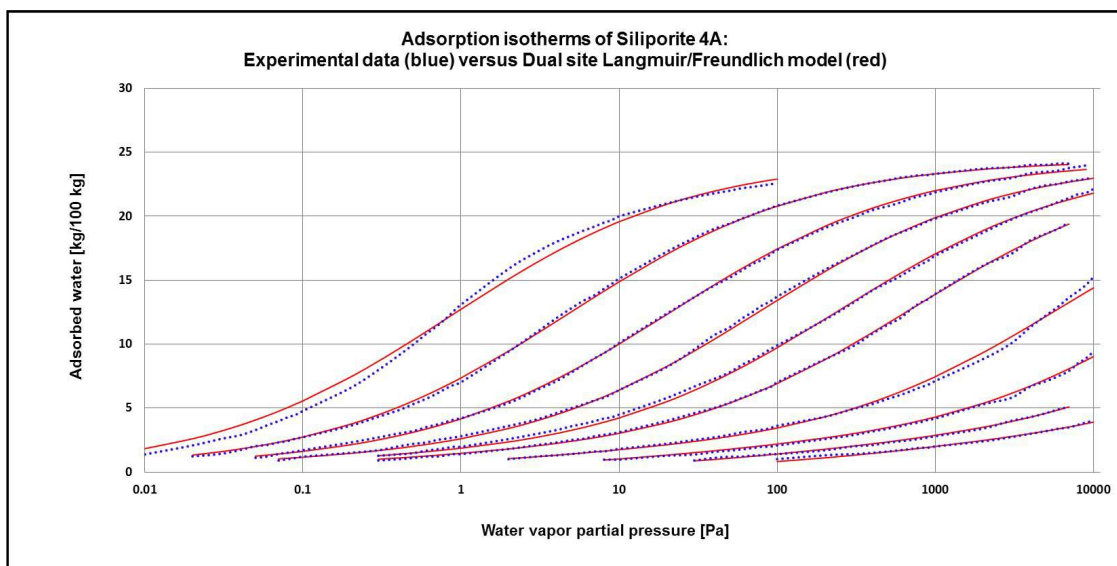


Figure 1: Fitting of Adsorption Isotherms for 4A molecular sieves

The overall CFD model developed was validated with experimental and industrial data, both for adsorption and regeneration phases. The detailed description of the model will not be further discussed, as the main objective of this article is to present the application of this CFD tool on several industrial cases.

3. FACTORS INFLUENCING DESIGN AND OPERATION

The use of molecular sieves to separate impurities is a reliable, proven and widely adopted technology in oil and gas industry. The adsorption process on molecular sieve is a complex phenomenon and often provides challenges while designing and operating the units due to a number of parameters that governs the efficiency of such processes. A wide range of operating issues in molecular sieve units can be caused by not only poor design decisions or deviations from design conditions but also mechanical and operational failures. These upsets can result in reduced lifetime, increased pressure drop across beds, loss of product quality, hydrate formation, increased system corrosion, or increased plant downtime, which ultimately have cost implications. For these reasons, it is extremely important to ensure that the molecular sieve units, firstly, are properly designed, and secondly, are operated with process equipment in good working order.

A number of parameters influence design and operation of molecular sieves. The operating temperature and partial pressure of an impurity along with the type of molecular sieve (3A, 4A, 5A, 13X) defines the adsorption capacity of that impurity. Flowrate and pressure drop constraints coupled with adsorption capacity are important to select an appropriate flow regime, mass transfer kinetics and, thus, design of vessels. An adapted pore size of molecular sieve along with an appropriate bed configuration (based on adsorbent size could be composed of big particles, small particles or a split bed) also influence the size of vessels. The choice of an appropriate diameter to height ratio will not only have influence on the pressure drop but also on regeneration duty requirement.

It is well known that molecular sieves age over time with each regeneration cycle. It is, thus, important to properly design and operate the regeneration phase. An incorrect pressure change rate can lead to

sub-zero temperatures resulting in ice formation and, thereby, damaging the molecular sieve structure. Channeling or lifting of bed can occur if an appropriate pressure drop per length is not respected. The heating step is the most crucial step of regeneration phase. Correct temperature ramps should be provided to avoid damage of the molecular sieves by thermal stress. An intermediate heating step is often recommended in drying applications to avoid the phenomenon of hydrothermal damaging of molecular sieve. An appropriate heating temperature adapted to the type of molecular sieve and sufficient heating time should be provided to attain a stable outlet temperature plateau at end of regeneration to mark the completion of regeneration. The type of regeneration gas (contaminants free, physical properties), flowrate and flow directions are equally important for an efficient regeneration.

Even though empirical models can address the majority of above parameters, operational issues and reduced adsorption efficiency can be caused by other parameters that require deep insight on hydrodynamics in addition to usual empirical models. One of these parameters is the presence of contaminants [3]. In olefin applications, coking is often problematic as it blocks the pores, reduces adsorption capacity and increases the pressure drop. Sometime liquid hydrocarbon carryover or condensation can lead to aggregates formation that result in not only reduced adsorption capacity and increased pressure drop, but also improper flow distribution and channeling problems. More frequent in natural gas applications, this latter problem arises also by liquid water carryover, salts carryover and hydrothermal damaging of molecular sieve. The presence of acidic or basic compounds (caustic, amines, low pH acids, CO₂, H₂S, etc.) can chemically attack the zeolite and the binder resulting in disaggregation of the molecular sieve structure (powdering). Figure 2 illustrates some pictures of molecular sieve subjected to these problems.



Figure 2: Impact on molecular sieve due to contaminants

A proper design of feed distributor (openings, distance from bed, fluid velocities) is often considered while designing an adsorption vessel. Operational issues can also arise due to support grid partial failure or leakage on the periphery of grid. All these parameters and a number of others like flow distribution, wall effects, etc. cannot be properly analyzed just by empirical models but require a robust CFD analysis in order to find an appropriate solution to reduce the capital and operational expenses.

The above list is certainly not exhaustive. The next chapter will illustrate a few examples that were analyzed using the CFD model. For the sake of simplicity, the adsorption vessel is described by using a 2D axisymmetric geometry.

4. CASE STUDIES USING CFD MODEL

This section will present results of some cases that were studied using the CFD model. For simplicity, only dehydration applications are considered. A base case (case 0) was simulated for a selected geometry and set of process conditions based on industrial data and will be used as a reference for comparisons with other cases. Breakthrough time is defined as the time required to reach the outlet impurity concentration specification. Breakthrough curves will be used to show the impact on adsorption capacity through the difference in adsorption time between each case studied and the base case.

4.1. Case 0: Base Case

This base case will be used to evaluate the impact of different parameters (different cases studied). The geometry and process conditions were selected based on an industrial unit (name not disclosed in article). A 4A molecular sieve was used. Figure 3 illustrates the design basis of this case.

The breakthrough times for this case when the outlet water content crosses 0.1 ppmV, 1 ppmV and 10 ppmV are 11.5 h, 13.7 h and 15.9 h, respectively. However, the breakthrough time corresponding to 0.1 ppmV will be used for comparison. The breakthrough curve and water adsorption concentration profiles across the bed at different given instants are illustrated in Figure 4.

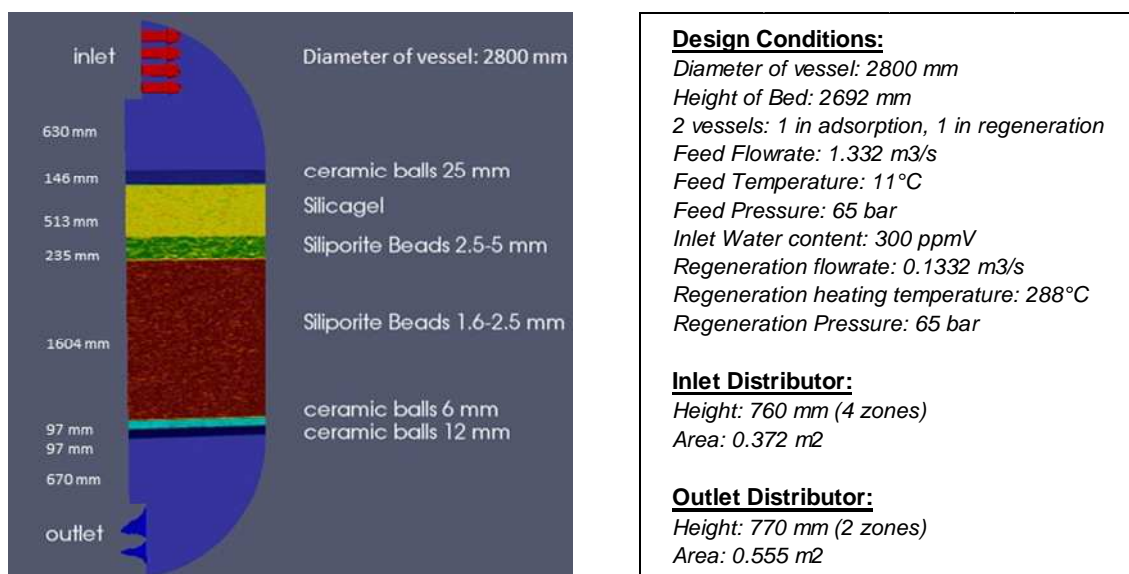


Figure 3: Design Basis for Base Case (Case 0)

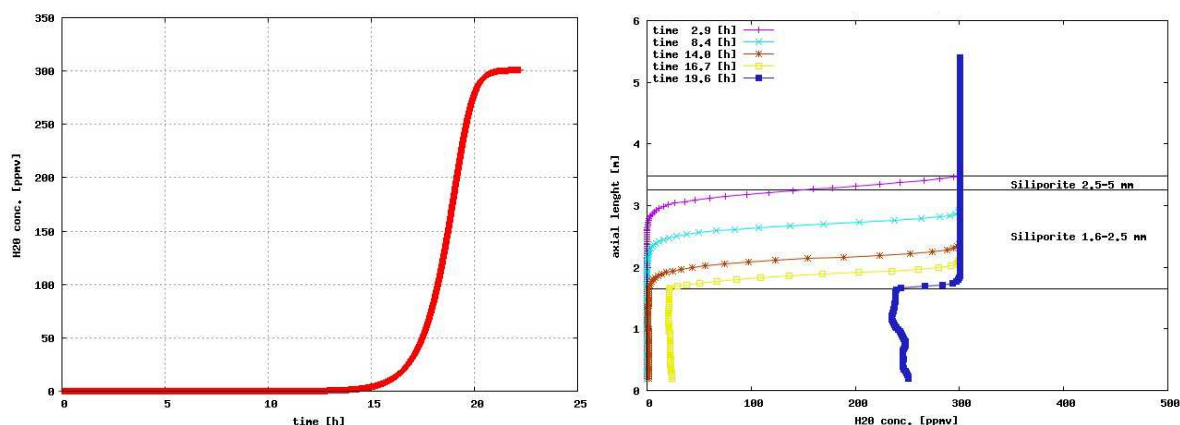


Figure 4: Breakthrough Curve and water adsorption profile across bed (Case 0)

4.2. Case 1: Distributor design and arrangement

The design of inlet distributor for gas is often considered as a crucial step by vessel manufacturer to minimize the impact of non-homogenous gas distribution and velocity profiles on the efficiency of adsorption on the molecular sieves.

Different designs are available in the market, more often a slotted cylinder type distributor is used. Several parameters are important to design like distance between the vessel inlet/outlet and the slotted cylinder, the diameter of the slotted cylinder, the cylinder height, the open area, the width of slots, the height of slots, the distance between the slots and, last but not the least, the distance between distributor and molecular sieve bed top layer. A distributor also creates pressure drop due to high velocity regime but this, obviously, does not influence performance of molecular sieve but is more of a consideration to be taken into account for compressor design.

Among the parameters mentioned above, the distance between distributor and molecular sieve bed top layer is often a subject of discussion as it impacts directly the capex (extra steel requirement due to extra height) and opex (extra regeneration duty requirement to heat this portion of steel). Further, in current oil and gas context, industry is looking for debottlenecking options and frequently wonders if this space between distributor and top bed layer can be utilized to put more molecular sieve, thereby,

increase the unit capacity without significant capital expenses. It is due to these facts that studying the impact of distributor design and arrangement using CFD was an obvious choice knowing that empirical models are incapable to answer this aspect.

4.2.1. Case 1A: Distance between distributor and top bed layer

It is often recommended that a minimum distance of 600 mm should be maintained. The base case (Case 0) was designed for a distance of 630 mm. In the present case (Case 1A), this distance was reduced to 150 mm.

Figure 5 demonstrates the profile of water content in gas. At the beginning, as expected, a non-homogenous profile was observed. Surprisingly, as the gas came in contact with ceramic balls and silicagel layer, the profile started to homogenize (due to distribution) and when the gas came in contact with molecular sieve, the profile was completely homogenous after less than 1 minute. The adsorption efficiency was same as the base case and the breakthrough time did not change. This means that the distance between distributor and bed top layer does not impact the adsorption performances. This is due to a very short residence time (~5s) compared to the breakthrough time for adsorption (11.5 hours). This indicates that the role of hydrodynamics in this case is insignificant compared to the phenomenon of adsorption. The gas velocity is about 1 m/s while the velocity of concentration front movement along the bed is about 10000 times slower. Secondly, the velocity profile adjust very quickly due to the high porous nature of molecular sieve.

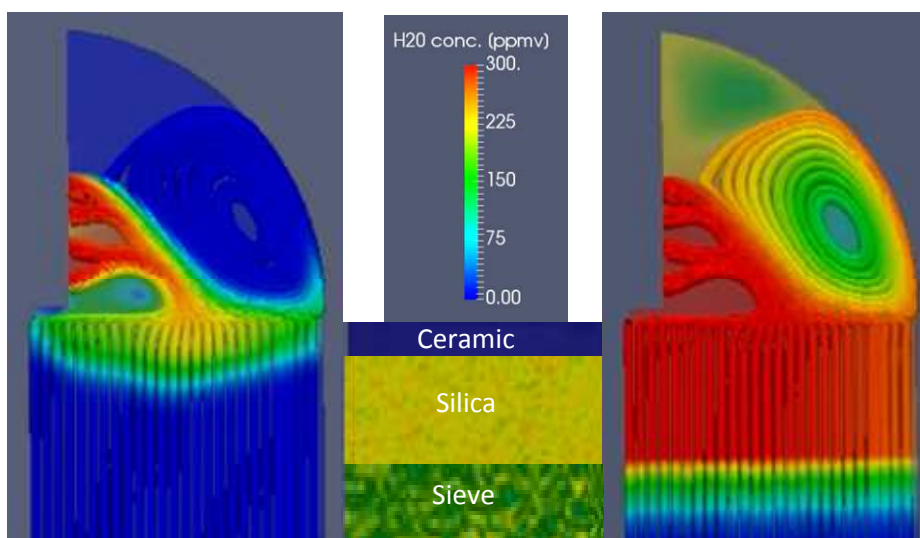


Figure 5: Water content in gas: Non-homogenous profile at beginning (left) and homogenous profile after 1 min (right) – Case 1A

Another simulation was performed by reducing further this distance from 150 mm to 80 mm and in addition to this, the bottom distributor distance was also reduced from 670 mm to 70 mm. Again, no difference with respect to the base case was observed in terms of adsorption performance. To further analyze this observation, two cases were studied:

4.2.2. Case 1B: Reduction of slot area

The slot area was drastically reduced to induce a high velocity gradient (higher velocity near the wall and low velocity at center). Figure 6 demonstrates the profile of water content in gas. At the beginning, as expected, a non-homogenous profile was observed. Again like for the above case, as the gas came in contact with ceramic balls and silicagel layer, the profile started to homogenize (due to distribution) and when the gas came in contact with molecular sieve, the profile was completely homogenous after less than 1 minute.

4.2.3. Case 1C: Gas injection with inserted pipe

Instead of the distributor, a simple pipe was used to inject gas in vessel that generated a velocity gradient (higher velocity at center and low velocity near the wall). Figure 7 demonstrates the profile of

water content in the gas. At the beginning, as expected, a non-homogenous profile was observed. Again, like for above cases, as the gas came in contact with ceramic balls and silicagel layer, the profile started to homogenize (due to distribution) and when the gas came in contact with the molecular sieve, the profile was completely homogenous after less than 1 minute.

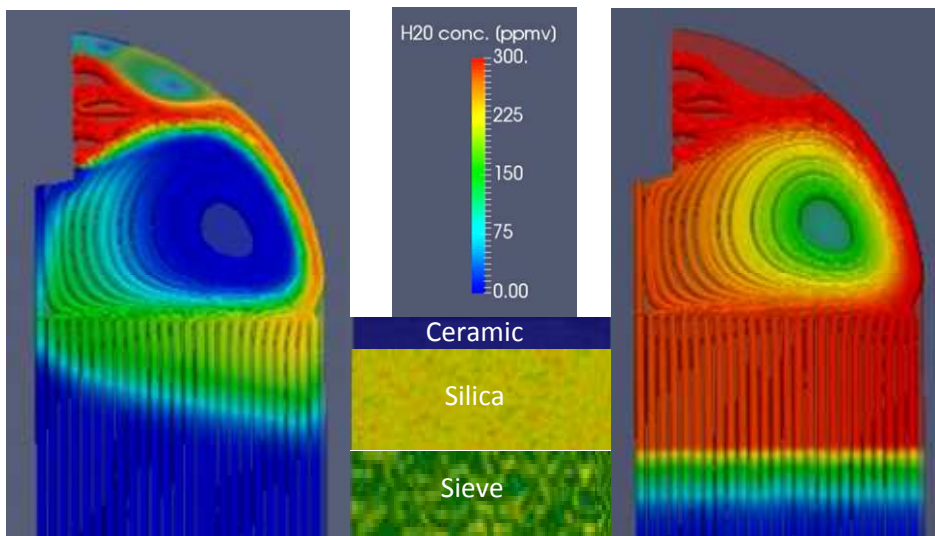


Figure 6: Water content in gas: Non-homogenous profile at beginning (left) and homogenous profile after 1 min (right) – Case 1B

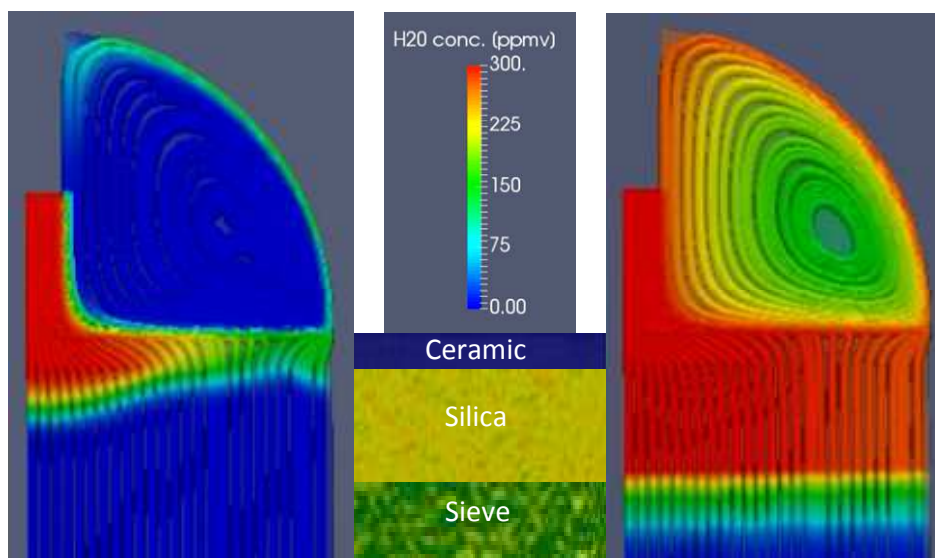


Figure 7: Water content in gas: Non-homogenous profile at beginning (left) and homogenous profile after 1 min (right) – Case 1C

This is an important result that contradicts the traditional knowhow. However, one aspect that was not part of this study but which plays important role is the impact of high velocities on the disruption of horizontality of the top layer of the bed. Thus, one should proceed with caution while considering to decrease the distance between distributor and top bed layer. If the velocities are in an acceptable range, the bed integrity is expected to be maintained and the distance between distributor and top bed layer can be reduced (savings for new vessel design and easy debottlenecking for existing vessels).

For Case 1A, the reduction of 480 mm of height resulted in a 9% reduction in steel quantity and a 4% reduction in regeneration duty for a new vessel design. For an existing vessel, this can represent about 25% increase in design flowrate by putting additional molecular sieve.

4.3. Case 2: Grid failure or Leakage

The integrity of a grid used to support an adsorbent bed and a proper sealing is mandatory for proper operation of molecular sieve units. Two cases were studied to analyze the impact of problems that may arise from grid.

4.3.1. Case 2A: Grid failure (inclination angle 20°)

One of the frequent operational issues arises when the grid joints break and the grid inclines, thereby, inclining the adsorbent bed. This may happen due to poor calculation of bed load, mechanical defaults of grid or poor welding/joints with vessel wall. In the present case, the grid was inclined by an angle of 20°, thereby, inclining the adsorbent bed, as illustrated on left side of figure 8.

At first, it was assumed that the incident was not abrupt and the bed porosity did not change. Interestingly, the adsorption performance was only slightly impacted (about 25 min difference in breakthrough time as compared to the base case) as illustrated by breakthrough curve on right side of figure 8.

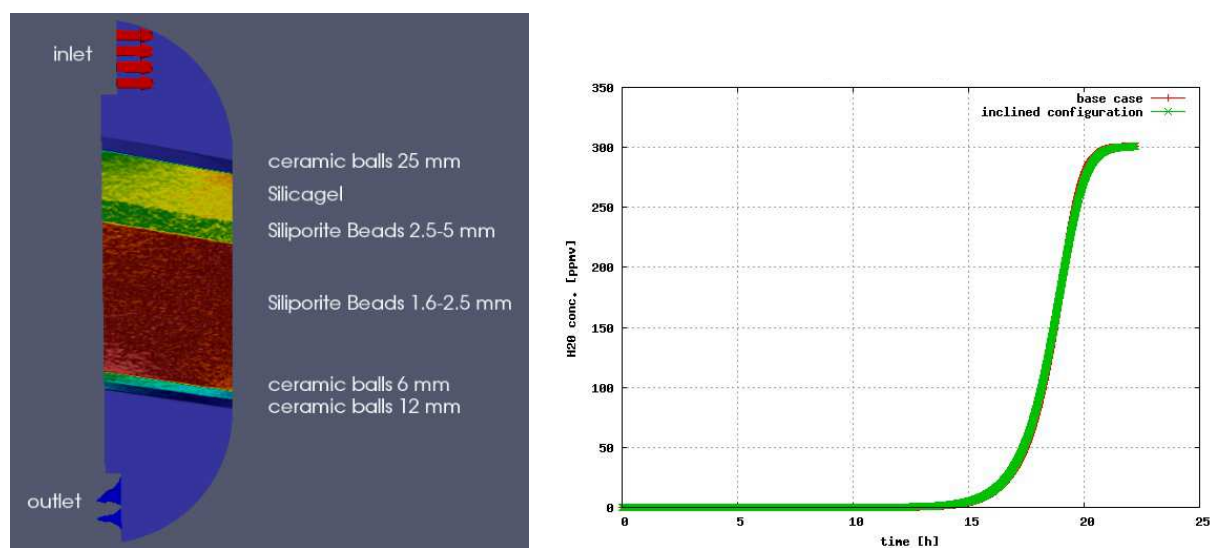


Figure 8: Grid failure (inclination by angle 20°)

Sometimes the incident, if happened abruptly, may induce a difference of bed porosity and bed disruption leading to preferential paths for gas in addition to some product loss and the impact on adsorption performance can be expected to be much worse.

4.3.2. Case 2B: Grid leakage due to defect in sealing

Another recurrent problem in industrial plant is grid leakage near the wall. This often happens if the grid is not properly sealed with ceramic ropes or the ceramic ropes degrade with time. Figure 9 illustrates the proper sealing of grid with ceramic ropes.

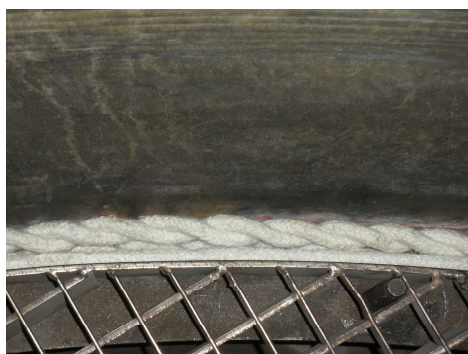


Figure 9: Sealing of bottom grid with ceramic rope

This leakage will result in severe wall channeling across the adsorption bed. To study this case, a bed porosity profile was imposed using Giese law^[18]. Figure 10 clearly illustrates that the impact of this operational issue can be drastic on adsorption performance. The breakthrough time was reduced from 11.5 hours for the base case to 2.4 hours for this case. Of course, the extent of impact depends on how severe is the problem, a worst-case scenario was simulated in the present case.

The impact of Case 2A is about 4% reduction in lifetime and about 7% increase in regeneration duty to compensate the impact of non-homogenous gas distribution. Further, a slight increase of pressure drop by 2% was observed.

Obviously, for the case 2B, an immediate reparation is required which can lead to a shutdown to unload/reload the molecular sieve and sometimes premature changeouts.

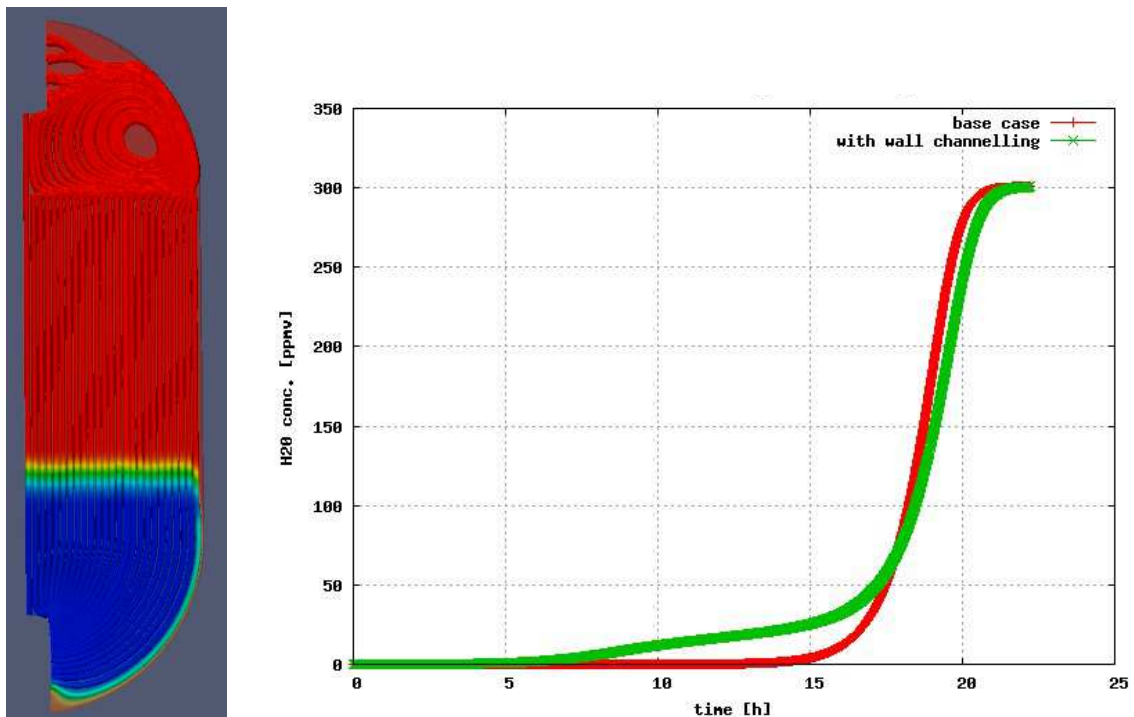


Figure 10: Early breakthrough due to grid leakage (wall channelling)

4.4. Case 3: Channeling during Regeneration

It is well known that there is always some residual water content left in molecular sieve bed after regeneration phase. The design and operation of regeneration phase will govern whether this residual water remains stable or increase, thereby, impacting capacity of adsorption in adsorption phase and, thus, lifetime of the molecular sieve. Regeneration flowrates are significantly lower as compared to the feed flowrates during adsorption phase, thus, more susceptible to fall into channeling regime. This channeling can result in incomplete regeneration in some parts of bed. Hence, sufficient flowrate and pressure drop per length are crucial parameters to avoid channeling in bed during regeneration phase, which can avoid rapid residual water build-up.

Empirical models often do not predict exactly this effect that results from flow distribution. A case was studied using the CFD model in which the breakthrough time of aged molecular sieves were compared for a 10 times lower regeneration flowrate (in channeling regime) as compared to the base case flowrate. As expected, the residual water build-up with lower regeneration flow was significantly higher as compared that for the base case and the breakthrough time decreased by about 1 hour.

Figure 11 illustrates three breakthrough curves, the red one with fresh molecular sieve, the green one with regenerated molecular sieve with appropriate flowrate and the blue one with molecular sieve regenerated with low regeneration flowrate in channeling regime. It is important to note that sometimes with this low regeneration flowrate (corresponding to channeling regime), no significant

reduction in residual water might happen even for longer heating time, especially when the regeneration pressure is very high.

The obvious impact of above issue due to the decrease of adsorption time (leading to an increase of number of cycles) is about 10% decrease in lifetime of molecular sieve. An increase of about 5% regeneration duty (increasing heating temperature and heating time) was required to limit the impact even though not that significantly.

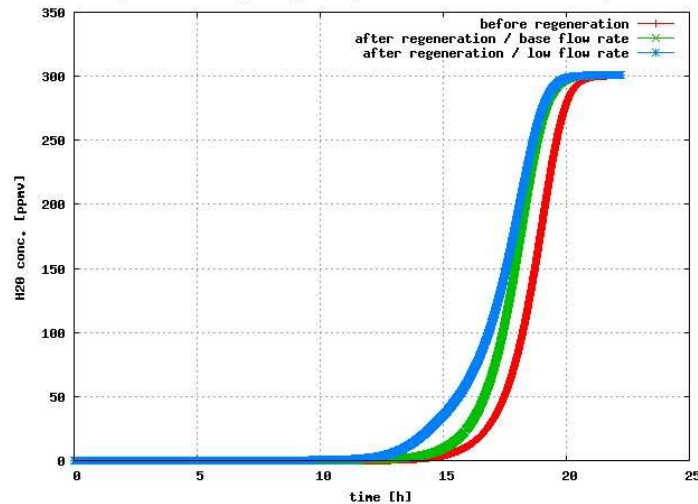


Figure 11: Channeling during regeneration phase

4.5. Case 4: Liquid Carryover

Another frequent operational issue arises due to liquid carryover. Droplets of liquid water are generally carried over onto the molecular sieve bed when the upstream gas-liquid separator experiences upset operating conditions, is undersized or not efficient enough. However, liquid water can also come from low points or dead volumes in the piping where vapor can condense to liquid during some phase of the process, waiting for the next switch to be entrained onto the bed. This not only concerns water, but also hydrocarbons. This carryover affects adsorption performance significantly. Obviously, more water has to be handled by the molecular sieves, which has an impact on the adsorption time, possibly leading to premature breakthrough. Water droplets strongly react with molecular sieves, both physically (adsorption heat release) and mechanically (hammering the structure). This results in local "hot spots" where the clay binder is damaged and powdered. In severe cases, dusting becomes significant, leading to pressure drop increase, channeling, and premature breakthrough.

The damage to molecular sieve often happens slowly and most of the time it is difficult to determine as how, where and to what extent the liquid carryover is happening. Sometimes, accidental upsets can result in bulk liquid carryover. In existing plants, often the extent of the impact and the mitigation steps are fully determined once the samples of molecular sieve bed are analyzed after a changeout.

A CFD simulation was performed for a case where the carryover led to a dead zone formation at the center of upper bed. Figure 12 shows the presence of this block of inactive molecular sieve (9% volume of total large beads and 2% volume of total small beads) and the profile of water content in gas when breakthrough happens. The breakthrough was observed at 9.1 hours as compared to 11.5 hours for the base case as illustrated in figure 13.

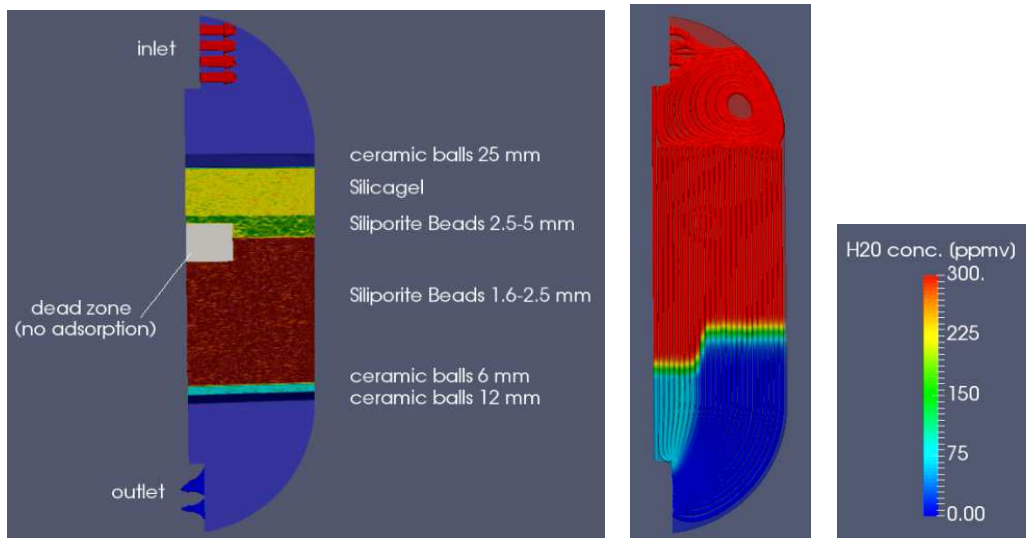


Figure 12: Impact of dead zones created by liquid carryover

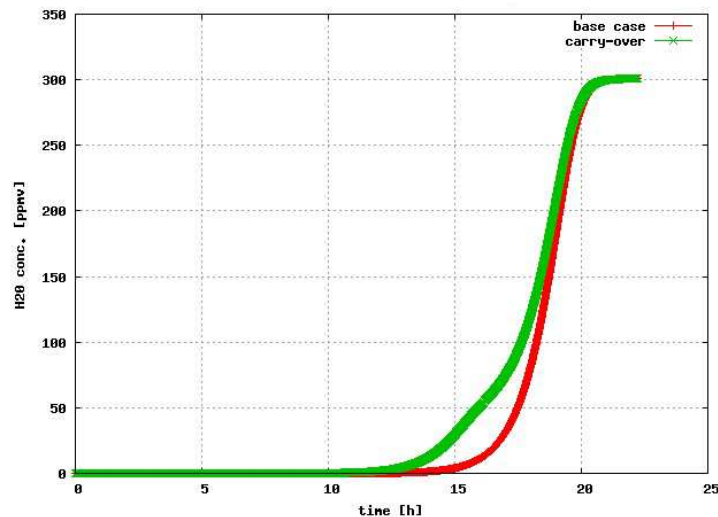


Figure 13: Early breakthrough due to dead zones created by liquid carryover

Case 4 shows a decrease of 2.4 hours of adsorption time (leading to an increase of number of cycles) meaning 25% reduction in lifetime of molecular sieve. Further, the pressure drop across the bed increased by about 15%.

4.6. Case 5: Retrocondensation

Another recurrent operational issue that happens during the regeneration phase is retrocondensation leading to hydrothermal damaging of molecular sieve. This phenomenon is well known and widely mentioned in literature^[3,16,17]. By heating too fast at a high temperature, water rapidly desorbs from the lower layers, while the bed experiences an important temperature gradient, i.e., its bottom is already hot, but its upper section is still at adsorption temperature (Figure 14). When arriving onto these colder parts of the bed, the regeneration gas gets oversaturated, and water “retro-condenses” on the top layers, especially near the vessel wall. This phenomenon can be seen on the outlet temperature curve of the regeneration gas that shows an inflexion (typical of a change of physical state). As the temperature increases, it soon results in boiling the water in the molecular sieve bed. This phenomenon is enhanced at high pressures and low regeneration flowrates.

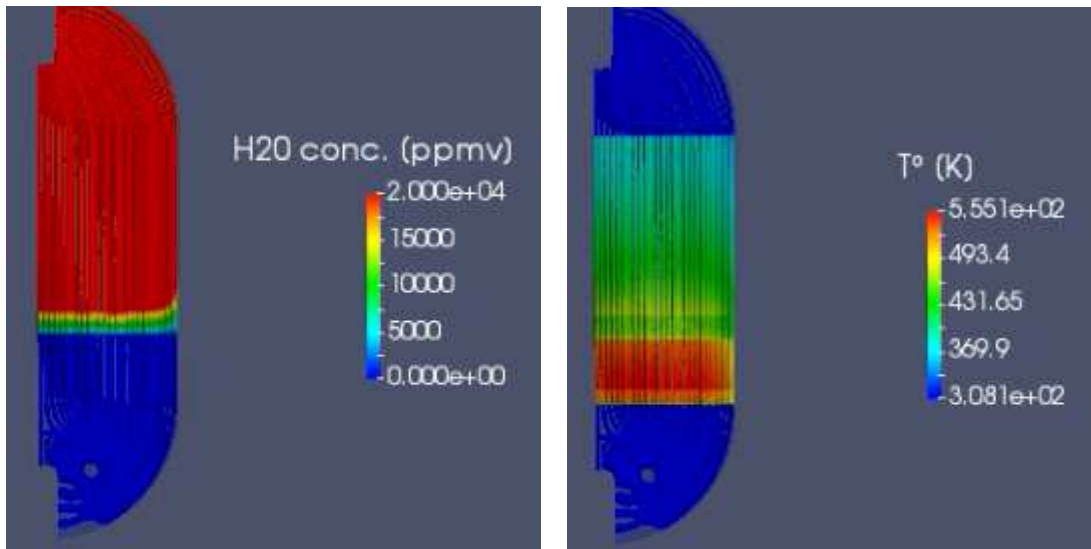


Figure 14: Regeneration gas water content (left) and Bed temperature gradient (right) after 1.5 hours of heating

The consequence of water condensation is obviously the weakening of the binder and of the zeolite structure. The binding clay is leached from the molecular sieve structure and disaggregates to dust and powder. Eventually, it also rearranges to form agglomerates all around the vessel under the action of water soluble salts that can ion exchange with the zeolite and cement the structure. In some cases, the agglomerates can take very significant volumes of the bed (donut formation), causing preferential paths and high pressure drop.

Empirical models are often limited in predicting the impact of this phenomenon. Only CFD models can precisely analyze and predict the impacts arising due to the complexity of hydrodynamics during this phenomenon. A CFD simulation was performed with aggregates formed (2.5% volume of total small beads) due to this phenomenon based on industrial inputs. Figure 15 illustrates the arrangement of these aggregates in the bed (left side). The impact on hydrodynamics (disruption of mass transfer profiles) and an early breakthrough is also illustrated (on the middle and right, respectively). The aggregates not only represent the loss of adsorption capacity but also their impact on mass transfer profile due to preferential paths is non-negligible. The breakthrough time obtained for this case was 10.4 hours as compared to 11.5 hours for the base case as shown in figure 16.

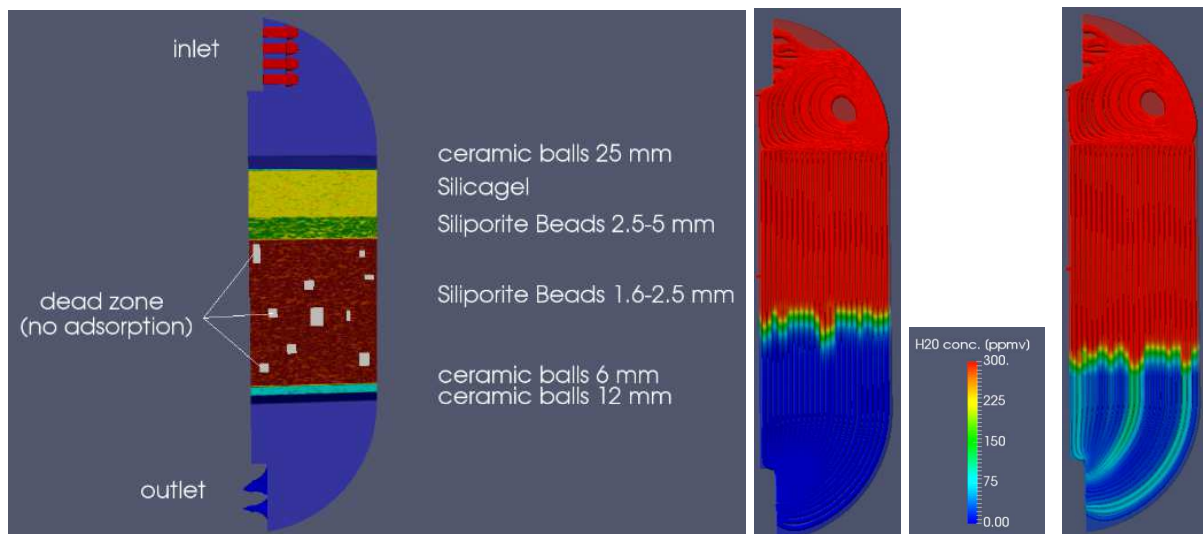


Figure 15: Dead zones created due to retrocondensation (left), disruption of MTZ (middle) and Early breakthrough (right)

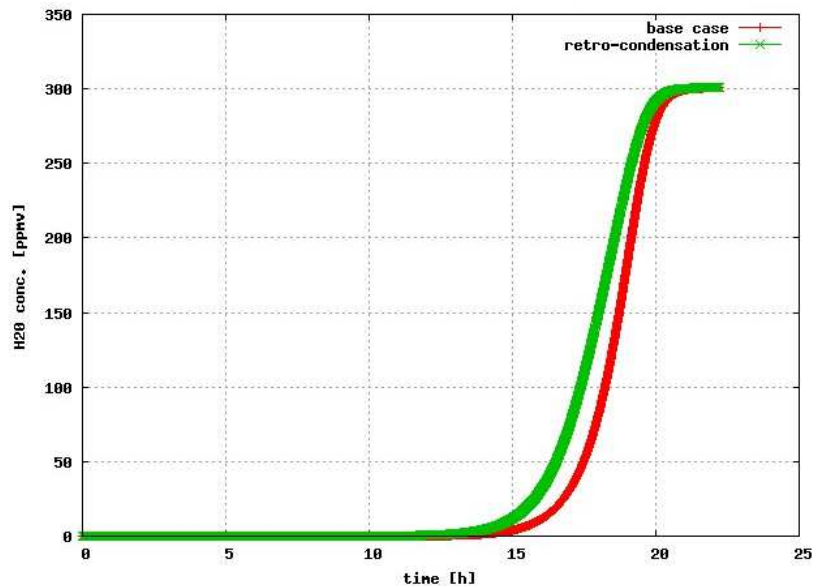


Figure 16: Early breakthrough due to retrocondensation

The obvious impact of the above issue for the case studied is about 13% decrease in lifetime of molecular sieve. Further, the pressure drop across the bed increased by about 8%. An increase of about 5% regeneration duty (increasing heating flowrate and heating time) was required to limit the impact even though not significantly.

4.7. Case 6: Use of Bottom Head for Debottlenecking and Vessel design optimization

The traditional design of molecular sieve vessels includes a bottom grid with a small cylindrical section followed by a bottom head. The space in this cylindrical section and bottom head is not utilized and, obviously, results in extra steel requirement (capex and opex implications). However, an interesting option to reduce capital cost and operational cost is to fill the bottom head with molecular sieve and ceramic balls. However, for long, industry has been reluctant to explore this option due to uncertainties of design and the complexity involved due to the change of the geometry at bottom section. One pertinent way to efficiently answer this excellent opportunity of debottlenecking and reducing capex/opex for new designs is through CFD simulation that integrates the impact of geometry on hydrodynamics and mass transfer characteristics.

4.7.1 Case 6A: Use of bottom head with exact quantities of adsorbent as in the base case

In the present case, the exact quantities of different adsorbents (molecular sieve, ceramic balls, silicagel) were taken as in the base case, however, the filling was done also in the bottom head. This reduced the height of the vessel by eliminating the unused cylindrical section and also the height required for molecular sieve and ceramic balls that were loaded inside bottom head. Figure 17 illustrates the new geometry (on left) and the mass transfer profile (on right) during breakthrough. We observe that the mass transfer profile was slightly impacted due the decrease of cross-sectional area resulting from bottom head. This resulted in a breakthrough at 10.8 hours instead of 11.5 hours for the base case as shown in figure 18. This means that an extra amount of molecular sieve will be required to compensate this impact.

4.7.2 Case 6B: Use of bottom head with slightly more quantities of adsorbent than in case 6A

This extra amount corresponded to about 45 mm of height in order to achieve same breakthrough time as the base case. Thereby, an overall gain of 510 mm of height could be achieved over the base case for same performance.

This gain represents about 10% saving in steel amount for vessel and about 4% gain in regeneration duty requirement as compared to the base case. Furthermore, for an existing unit, a debottlenecking

can be performed to about 30% of more flowrate with respect to the base case. No significant impact on pressure drop was observed.

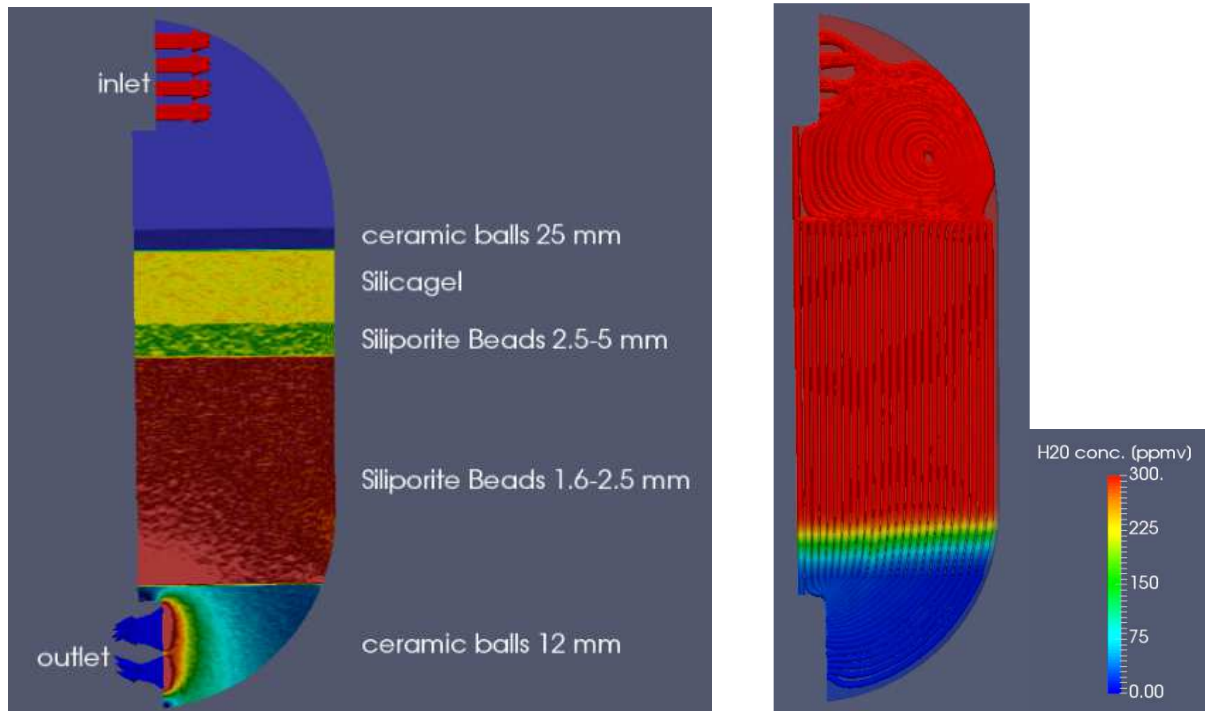


Figure 17 : Use of bottom head (on left) and the mass transfer profile (on right) during breakthrough

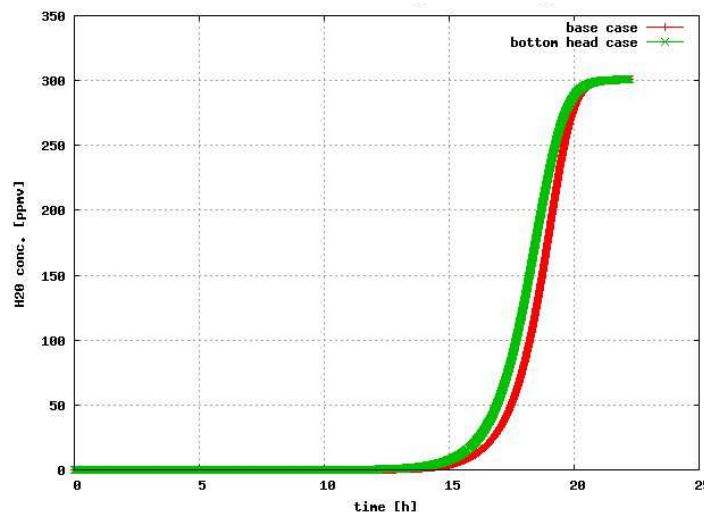


Figure 18: Breakthrough while using bottom head with same quantity of adsorbent as the base case

4.8. Case 7: Coking

As mentioned earlier, molecular sieve ages with time and its capacity slowly decreases. One of the main reason is that the porosity gets partially fouled with heavy carbonaceous components. These compounds, often referred to as “coke”, are caused by heavy hydrocarbons (HC) present in the feed and which sometimes remain in the bed along the cycles. The mass transfer zone is lengthened and the overall porosity is decreased. Normal fouling is taken into account in the unit design, among many other factors that define the product “ageing” rate. However, in some cases, fouling is much more important than anticipated, leading to premature breakthrough. The real issue is that a part of the deposit is not removed during regeneration and is subject to cracking and “polymerization”. It ultimately forms heavy growing carbonaceous deposits that build up in the porosity^[3,15], especially at zeolite acidic sites.

Samples from industrial unit often helps to evaluate the exact impact of this coking. Based on such experience, a CFD simulation was performed where the presence of coke reduced the adsorption capacity by blocking the pores. A 3A molecular sieve was used with same geometry and process conditions as the base case. Figure 19 illustrates the breakthrough curves comparison with the base case. The breakthrough time decreased to 8.7 hours as compared to 15.9 hours for the base case.

The obvious impact of above issue is about 27% decrease in lifetime of molecular sieve. An increase of about 4% regeneration duty (increasing heating temperature and heating time) was required to limit the impact even though not that significantly. The pressure drop increased by 24%.

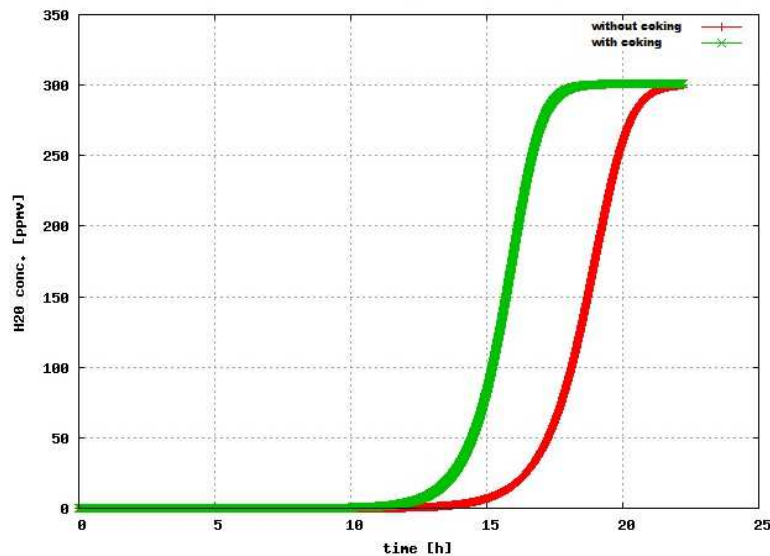


Figure 19: Impact of coking of porosity

4.9. Case 8: Effect of molecular sieve bead sizes

One of the important parameters when designing molecular sieve bed units is the choice of beads or pellets size. Typically, two sizes are used in industry, small size (1.6-2.5 mm for beads and 1.6 mm for pellets) and big size (2.5-5 mm for beads and 3.2 mm for pellets). However, depending on the application and design constraints, a molecular sieve supplier can choose only large size or only small size or even a split bed composed of large size and small size. The difference lies in the fact that large size adsorbent provide lower pressure drop but on the other hand have longer mass transfer zone (thereby more quantity is required) as compared to small size adsorbents. Frequently, a split bed is an optimum solution with big size adsorbent in equilibrium zone (as this is a volume phenomenon, i.e., the molecular sieve is completely saturated) and small size adsorbent in mass transfer zone (as this is a surface phenomenon, i.e., the molecular sieve is saturated only on the surface).

The importance of CFD lies in the precise characterization of the difference in the mass transfer zone between difference sizes. A case is presented where the base case bed was either completely replaced by small size beads (Case 8A) or completely replaced by large size beads (Case 8B) as shown in figure 20. It is clear that the breakthrough time did not change for Case 8A with only small beads. However, the breakthrough time decreased to 3.7 hours for Case 8B when only large beads were used (figure 21). This is due to the fact that the mass transfer zone required for large beads was about 2 times (see figure 22) more longer than that for small beads and thus the quantity of molecular sieve in given bed volume was not sufficient.

Using the large beads alone (Case 8B) would thus require a bigger quantity of molecular sieve (about 1.3 m more height) as compared to the base case where a split bed was used. This can increase steel requirement by 26% and an increase in regeneration duty requirement by 20%. Furthermore, the decrease in pressure drop due to the large beads was largely offset by the increase in pressure drop due to high quantity of molecular sieve (an overall increase of 10%).

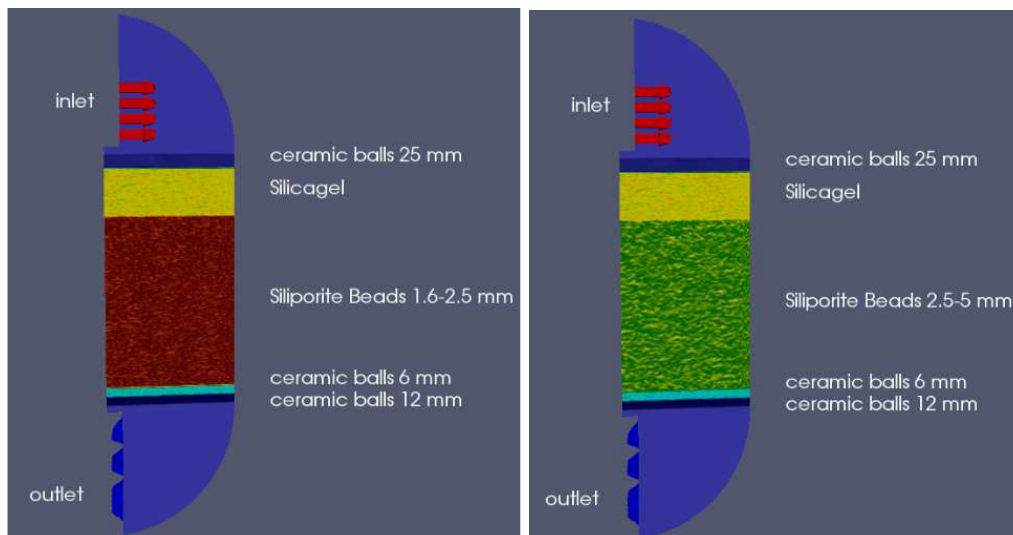


Figure 20: Bed composed of small beads – on left (Case 8A) and large beads – on right (Case 8B)

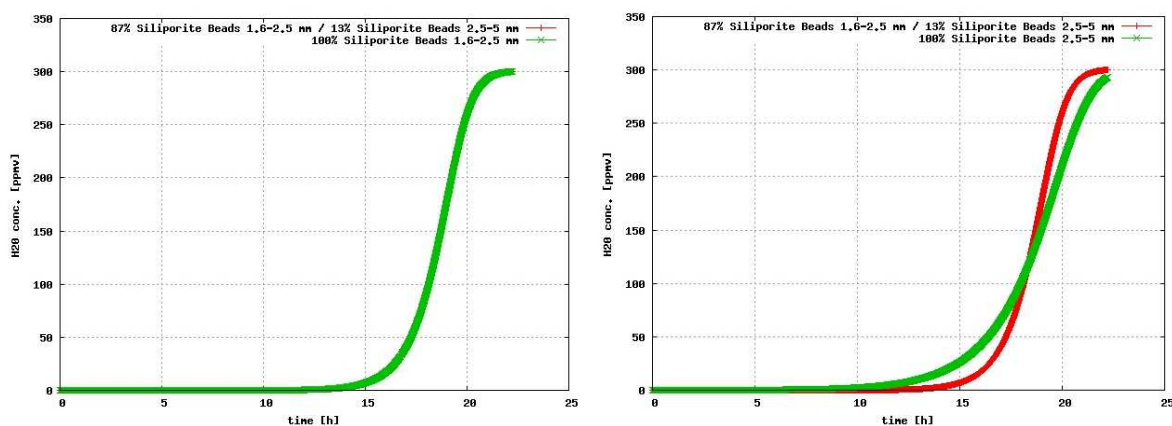


Figure 21: Breakthrough time – on left (Case 8A) and– on right (Case 8B)

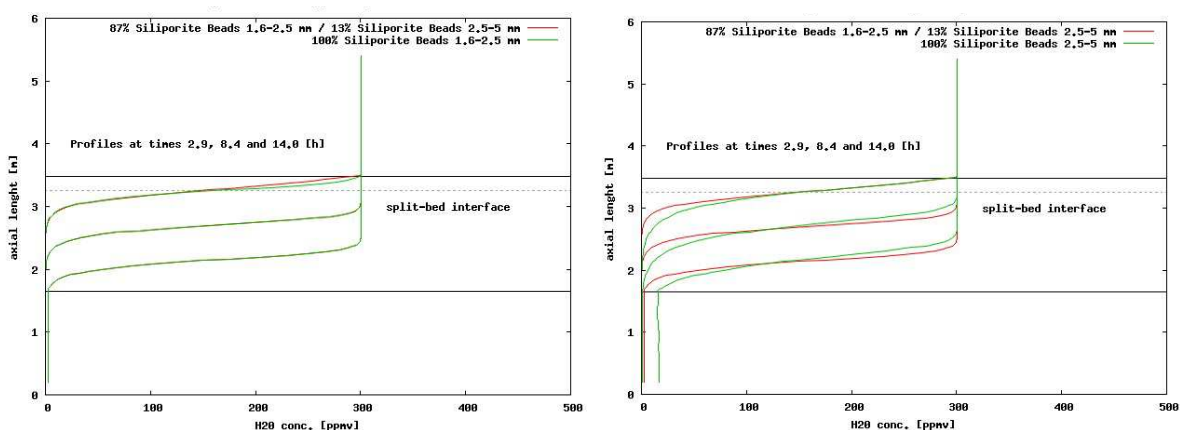


Figure 22: Mass transfer Profiles – on left (Case 8A) and– on right (Case 8B)

Table A summarizes the breakthrough time for different cases discussed in this article. The breakthrough time corresponding to an outlet concentration of 0.1 ppmV (used in article), 1 ppmV and 10 ppmV are provided.

Table A: Comparison of breakthrough time for different cases

Test Case	BT(0,1 ppm) [h]	BT(1 ppm) [h]	BT(10 ppm) [h]
Case 0	11.5	13.7	15.9
Case 1A	11.3	13.6	15.8
Case 1B	11.4	13.6	15.9
Case 1C	11.5	13.7	15.9
Case 2A	11.1	13.4	15.7
Case 2B	2.4	5.2	9.3
Case 3	9.1	11.4	13.4
Case 4	9.1	11.4	13.8
Case 5	10.4	12.5	14.8
Case 6A	10.8	13.0	15.4
Case 6B	11.5	13.7	15.9
Case 7	8.7	10.8	12.9
Case 8A	11.5	13.7	15.9
Case 8B	3.7	8.6	13.3

Table B shows a summary of major impact on capex and opex for the different cases. It is to be noted that these impacts correspond to cases described in the article and the degree of any impact may change in different situations. The values are represented in percent increase or decrease with respect to reference case (base case – case 0). Only key parameters are taken and all cost (capex and opex) associated around these individual parameters are variable depending on a number of factors (global context, purchasing, labor cost, unit set-up, country, currency, etc.). This article will not cover this in detail.

Table B: Impact through key parameters on Capex/Opex cost and debottlenecking opportunity for different cases

		Case 0	Case 1A	Case 1B	Case 1C	Case 2A	Case 2B	Case 3	Case 4	Case 5	Case 6A	Case 6B	Case 7	Case 8A	Case 8B
CAPEX	New Unit - Steel Saving	Ref.	-9%	0%	0%	0%	0%	0%	0%	0%	-11%	-10%	0%	0%	26%
	Lifetime	Ref.	0%	0%	0%	-4%	-100%	-10%	-25%	-13%	-10%	0%	-27%	0%	0%
OPEX	Regeneration duty	Ref.	-4%	0%	0%	7%	0%	5.0%	0%	5.0%	-4%	-4%	4.0%	0%	20%
	Regeneration Pressure drop	Ref.	0%	0%	0%	2%	0%	0%	15%	8%	0%	0%	0%	5%	10%
	Adsorption Pressure drop	Ref.	0%	0%	0%	2%	0%	0%	15%	8%	0%	0%	24%	5%	10%
	Changeouts frequency	Ref.	0%	0%	0%	4%	100%	10%	25%	13%	10%	0%	24%	0%	0%
DEBOTTLENECKING		Ref.	25%	0%	0%	0%	0%	0%	0%	0%	25%	30%	0%	0%	0%

5. CONCLUSIONS

A robust modelling framework within an open source CFD platform using Open FOAM software was developed. The model parameters were adjusted with more accurate adsorbent properties, isotherms and other data. The model was validated with experimental and industrial data, both for adsorption and regeneration phases. The utility and strength of CFD modeling was demonstrated through simulation of several cases. These cases covered ways to optimize the molecular sieve bed designs through insight on bed configuration, hydrodynamics and other process parameters. Other cases addressed the issues that concern troubleshooting, optimizing and adapting the plant operation under different constraints. Moreover, some cases provided interesting debottlenecking opportunities. The

impact on the key parameters governing capex and opex was also presented. It is clear that the use of CFD model has a significant supplementary role to play over empirical models to optimize capital and operational costs of both new and existing facilities, the latter being a major challenge for industrial operators and EPC firms in current global Oil and Gas context. For years, CECA has developed innovative solutions covering products, processes and services to help achieve this challenge. CECA will further continue the development and enrichment of this CFD model. This model has already and will continue to prove beneficial for the industry.

6. REFERENCES

1. R. Trent, "Dehydration with Molecular Sieves", *51st Laurance Reid Gas Conditioning Conference*, Norman, Oklahoma, February 2001.
2. Grace Davison, "Effects of Contaminants on Molecular Sieves", <http://www.offenbar-energy.com/pdf/EFFECTS%20OF%20CONTAMINENTS.pdf>.
3. A. Terrigeol, "Molecular Sieves Contaminants: Effects, Consequences and Mitigation", *GPA Europe Annual Conference*, Berlin, May 2012.
4. R.R. Eguren (BP America production Company), "Molecular Sieves operational challenges", *62nd Laurance Reid Gas Conditioning Conference*, Norman, Oklahoma, February 2012.
5. P. Meyer, "Molecular Sieves Troubleshooting", *GPA Europe Annual Conference*, Lisbon, September 2010.
6. H. G. Weller, G. Tabor, H. Jasak, and C. Fureby, "A tensorial approach to computational continuum mechanics using object-oriented techniques", *Journal of Computational Physics*, 12(6) :620–631, November 1998.
7. ED Dendy, NT Padiál-Collins, and WB VanderHeyden, "A general-purpose finite-volume advection scheme for continuous and discontinuous fields on unstructured grids", *Journal of Computational Physics*, 180(2) :559–583, 2002.
8. M Nordlund, M Stanic, AK Kuczaj, EMA Frederix, and BJ Geurts, "Improved piso algorithms for modeling density varying flow in conjugate fluid–porous domains", *Journal of computational Physics*, 306 :199–215, 2016.
9. M Gholami and MR Talaie, "Investigation of simplifying assumptions in mathematical modeling of natural gas dehydration using adsorption process and introduction of a new accurate Idf model", *Industrial & Engineering Chemistry Research*, 49(2) :838–846, 2009.
10. M Gholami, MR Talaie, and S Roodpeyma, "Mathematical modeling of gas dehydration using adsorption process", *Chemical Engineering Science*, 65(22) :5942–5949, 2010.
11. Damien Leinekugel-Le-Cocq, "Contribution à la modélisation dynamique simplifiée d'un procédé d'adsorption modulé en pression (P.S.A)", *PhD thesis, Université Claude Bernard, Lyon I.*, 2005.
12. Jürgen U Keller and Reiner Staudt, "Gas adsorption equilibria : experimental methods and adsorptive isotherms", *Springer Science & Business Media*, 2005.
13. Lian-Ming SUN and Francis MEUNIER, "Adsorption. aspects théoriques", *Techniques de l'ingénieur. Génie des procédés*, 2(J2730) :J2730–1, 2003.
14. Ralph T Yang, "Gas separation by adsorption processes", *Butterworth-Heinemann*, 2013
15. B. Wang, "Zeolite deactivation during hydrocarbon reactions: characterisation of coke precursors and acidity, product distribution", *Thesis University of London*, December 2007
16. P.B.C. Meyer, "Hydrothermal Damaging of Molecular Sieves and how to prevent it", *Gas Processors Association Europe*, Paris, France, February 2003.
17. M. Suckow, W. Lutz, J. Kornatowski, M. Rozwadowski and M. Wark, "Calculation of the hydrothermal long-term stability of zeolites in gas-desulphurization and gas-drying processes", *Gas Separation & Purification*, Vol 6 No.2, 101-108, 1992.
18. Augier, F., Laroche, C., & Brehon, E. (2008), "Application of computational fluid dynamics to fixed bed adsorption calculations: effect of hydrodynamics at laboratory and industrial scale", *Separation and Purification Technology*, 63(2), 466-474.