# Production of Pipeline Quality Natural Gas With the Molecular Gate™ $CO_2$ Removal Process

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## Abstract

In May of 2002, the first *Molecular Gate ä–Carbon Dioxide Removal* system for the removal of carbon dioxide and water was started-up at the Tidelands Oil Production Company operated facility in Long Beach, California and continues operation today. The feed source for the unit is hydrocarbon rich, water-saturated, associated gas from water flood enhanced oil recovery operations. The feed $CO_2$ concentration varies widely and is typically over 30% while the unit reduces the carbon dioxide level to less than 2%. The unit removes the carbon dioxide, heavy hydrocarbons and water producing pipeline specification gas for sale to the local natural gas utility company.

## Introduction

The first *Molecular Gate-Nitrogen Rejection* system operated for over two years removing 18% nitrogen from glycol dehydrated wellhead gas while producing pipeline specification product at an unattended site at Hamilton Creek in Southwest Colorado prior to the commercial system for Tidelands.

The Molecular Gate adsorbent used at Hamilton Creek facility is from a new family of titanium silicate molecular sieves with the unique ability to be manufactured with a desired pore size, in the case of Nitrogen Rejection with a 3.7-Angstrom pore. This pore size permits nitrogen (3.6 angstrom) to enter the pore while the larger methane molecule (3.8 angstrom) does not fit within the pore and passes through the fixed bed of adsorbent at high pressure. In this manner the system is similar to fixed bed dryers where water is adsorbed from the natural gas feed with the dry product produced at high pressure.

The adsorbent is utilized in a pressure swing adsorption system consisting of carbon steel adsorber vessels and a valve and piping skid network alongside the skid to control the feed, product and tail gas flows between the adsorber vessels. Adsorption occurs at high pressure, typically at 100 psig, and in the case of the Hamilton Creek unit at 400 psig, with the adsorbed nitrogen removed through a single stage vacuum pump and discharged at low pressure.

The Hamilton Creek system is operated by the pumper responsible for the gas wells through a daily visit to the site. Under these conditions it has achieved an excellent level of reliability and has been available for 99% of the time. No major issues have been identified with the system and trips are mostly attributed to valve and instrumentation drift or failure. The pumper can normally repair and restart the system within 15 minutes of his arrival to the site.

Since the start-up of the Hamilton Creek system thirty projects are underway for nitrogen rejection and carbon dioxide removal or both.

## Carbon Dioxide Removal

One of the initial advantages recognized for the nitrogen rejection technology is that carbon dioxide (3.4 Angstroms) is a smaller molecule than nitrogen and can easily be removed when present in a system designed for nitrogen removal. This co-removal of carbon dioxide is attractive to project economics and operation since it eliminates the need for a separate amine treating unit.

Pressure swing adsorption systems have, in a few instances, been used for the bulk removal of carbon dioxide from methane, such as through the use of activated carbon adsorbent. The advantages of PSA are in its simplicity but the technology is limited by a relatively low selectivity between methane and carbon dioxide using conventional adsorbents. This means that a large amount of methane is co-adsorbed along with the carbon dioxide leading to high losses of methane into the tail gas and larger adsorbent inventories.

The low selectivity of carbon dioxide over methane has been addressed in the *Molecular Gate – Carbon Dioxide Removal* system through the tailoring of the pore sizes of the adsorbent and designing for a low methane adsorption level on the adsorbent. Using a single stage vacuum pump for regeneration as well as a recycle to feed of a methane rich stream further enhances this inherent adsorbent selectivity to provide high methane recovery rates.

The carbon dioxide removal application was not initially targeted for Molecular Gate technology, but in mid-2001 Tidelands requested the removal of carbon dioxide from a heavy hydrocarbon rich associated gas stream at their Long Beach, California facility. In response to this request (and a few earlier requests) pilot plant studies were performed and a preliminary design prepared. The system was awarded in late 2001 and delivered to the site in about 16 weeks and continues to operate with no loss in performance to date.

The system offers a new route for the removal of bulk levels of carbon dioxide using proprietary adsorbent that has a high affinity for carbon dioxide while having a low capacity for methane. The system has advantages over the traditional amine and membrane processes for certain applications. It is ideally suited for coal bed methane, landfill gases and biogas and is appropriate for a wide range of conditions.

## Tidelands Long Beach, CA Facility

The majority of the hydrocarbon resources in the southern portion of the Wilmington oil field are owned by the State of California and the City of Long Beach, California. Production facilities are operated by Tidelands Oil Production Company. The giant Wilmington Oil Field has been a prolific producer of oil since its discovery in the early 1930's. Today the field's production is maintained through a water flood EOR operation. The location is challenging for oil and gas production with a need to address environmental and operational concerns in an urban location. Maintaining ground surface levels and oil production requires the removal and subsequent rejection of 200,000 b/d of total liquids of which 6500 b/d is oil. Along with the oil 1.5 MM SCFD of associated natural gas is produced.

The associated gas is contaminated with carbon dioxide at over 30% and also includes a smaller level of nitrogen and a large quantity of heavy hydrocarbons. It is produced at about 20 psig. In the facility a portion of the associated gas is used as fuel to operate internal combustion engines and other facility equipment. The local fuel consumption leaves over 0.5 MM SCFD of excess fuel that has previously been flared.

Tidelands staff of over 100 individuals is focused on the environment and safe operations. Upgrading the contaminated associated gas to pipeline quality was a highly desirable goal, however, distracting the ongoing operations with a complex facility, or one that could compromise the environment, was not acceptable.

## System Design

The Molecular Gate Unit at Tidelands is a relatively small system that treats about 1.0 MM SCFD of the associated gas.

Even at this small size the elimination of flaring and revenue generated through the sale of the pipeline quality gas to the local gas utility company allowed an acceptable return for the project.

One challenge in the design was the level of nitrogen contained in the feed stream. Since the gas utility company originally imposed a total inert specification of 4% and the system is not designed to remove nitrogen, excess nitrogen in the feed could lead to the system being non-compliant with the pipeline specification even if carbon dioxide was completely removed. This concern was addressed by reducing nitrogen sources.

The contaminated associated gas is split into a compressed stream for feed to the Molecular Gate unit and a bypassed stream. In the Molecular Gate unit $CO_2$, water and heavy hydrocarbons are removed and pipeline quality gas is produced. This pipeline quality gas is metered and sold.

The Molecular Gate adsorbents allow modification of one or more properties. These can include the pore sizes, cations exchanged into the adsorbent or the amount of binder. Such modifications change the adsorption of the targeted molecules or other feed components. In feeds containing heavier hydrocarbons the adsorbents can remove heavy components, mostly by adsorption onto the surface of the adsorbent or where a compound bed of adsorbents is used where a weak adsorbent is used to protect from water or the heaviest hydrocarbons. The adsorbent can also be designed to pass a level of the C2 and C3 into the product stream. The compound bed of adsorbents used at Tidelands adsorbs the water and heavier hydrocarbon components and removes them to the tail gas since there is a use for the tail gas as fuel.

The design and typical operation is shown in Table 1.

| | Design Feed | Actual Feed | Design Product | Actual Product |
|---|---|---|---|---|
| Flow, MM SCFD | 1.0 | 1.4 | 0.52 | 0.54 |
| Pressure, psig | 65 | 70 | 63 | 68 |
| Temperature, F | 60-80 | 60-80 | 60-80 | 60-80 |
| Composition, Mol % | | | | |
| C1 | 71.25 | 48.35 | 95.09 | 94.17 |
| O2, ppmv | 400 | 800 | 700 | 1500 |
| N2 | 2.18 | 1.34 | 3.74 | 2.40 |
| $CO_2$ | 18.82 | 37.58 | 0.19 | 1.90 |
| C2 | 2.35 | 2.96 | 0.90 | 0.68 |
| C3 | 2.12 | 3.77 | 0.20 | 0.03 |
| C4 | 1.75 | 3.11 | - | - |
| C5 | 0.76 | 1.40 | - | - |
| C6+ | 0.72 | 1.41 | - | - |
| $H_2O$ | Sat'd | Sat'd | - | - |

**Table 1 – Tidelands Design and Actual Performance Comparison**

The low-pressure tail gas from the Molecular Gate unit contains the $CO_2$, water and heavy hydrocarbons and is blended with the portion of the contaminated associated gas bypassed around the unit. This combined stream provides fuel for gas engines driving pumps that reinject water into the formation. A schematic of the flow balance is shown in Figure 1.

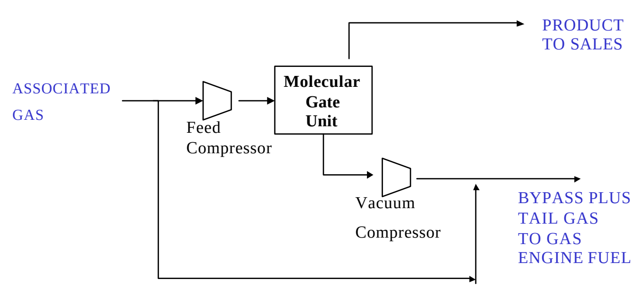


**Figure 1 – Tidelands Process Flow Schematic**

The operation and start-up of the Tidelands unit resulted in a few unexpected developments. The feed stream $CO_2$ level typically operates at about twice that of the design rate (37% versus 18%). While the unit is still able to operate at full capacity, some portion of this capacity was gained by the relaxation of the product specification such that up to 2% $CO_2$ is permitted into the product stream as compared to the design level of less than 2000 ppm.

In other respects the start-up was uneventful and from feed-in to normal, unattended operation, the time required was a few days. It is desirable to operate the unit continuously and this has generally been the case since start-up with on-stream factors over 99%.

Operating difficulties have been fairly minor. One modification made to the unit shortly after startup was to place additional pressure control between the feed compressor and the unit to minimize swings in the discharge pressure of the feed compressor. Although such pressure swings are not problematic for the Molecular Gate Unit, they were causing oscillating loads on the feed compressor.

The unit required the reactivation of an old pipeline, whose scale caused the blockage of filters and which was cleared up through further use.

The tail gas vacuum compressor has provided good operation. Vacuum compressor suction pressure was raised at startup to allow for higher discharge pressures at the vacuum compressor outlet. This was required as downstream consumers (I.C. engines and/or flares) were running at higher than design pressure. Tidelands strategy on startup of the Molecular Gate unit was to get the unit running then adjust downstream operations to optimize performance of the Molecular Gate Unit. In some cases this meant removing duplicate pressure regulators on IC engines so they could operate on a lower supply pressure, and in other cases it meant lowering the regulated pressure. In addition some units required tuning for the different quality fuel gas. Within a few days from startup the discharge pressure was lowered and the suction to vacuum compressor was also subsequently lowered.

The unit has operated for over six years and continues to operate with no changes in performance noted. Recently an automatic product purity control has been added to maintain the product at 2% carbon dioxide.

Tidelands continues to optimize the facility and recently installed a new gas engine driving a water injection pump which has reduced the excess fuel routed to the Molecular Gate unit and decreased the quantity of gas sold to the pipeline. Taking advantage of the unit's current excess capacity may allow the opening of currently shut-in high $CO_2$ wells.

**Figure 2 - Tidelands Molecular Gate System**

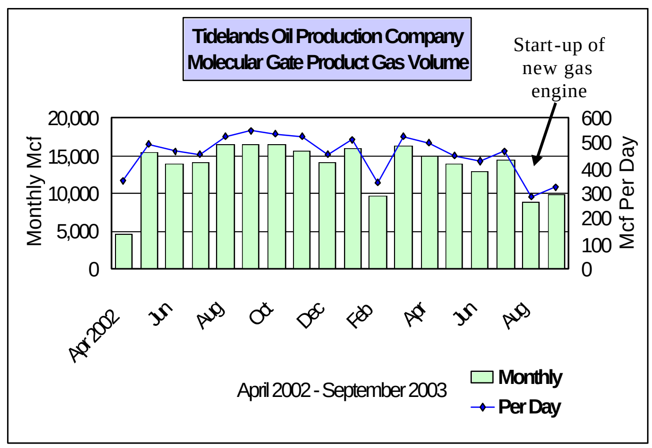


**Figure 3 - Tidelands Molecular Gate System**

The carbon dioxide removal requirements at Tidelands are somewhat unique. The main difference compared to typical field operations is a relatively low operating pressure and the local use for a large quantity of fuel. This fuel demand provides a convenient outlet for the tail gas from the Molecular Gate Unit but also means that the system need not achieve high methane recovery rates. At the Tidelands site the methane recovery rate is about 75%; acceptable for Tidelands but insufficient for most field operations where recovery rates in the 95% range are a more typical target. Recovery rates in the mid-90's are achieved through the addition of a methane vent recycle that recovers methane otherwise lost into the tail gas.

## Applications - Coal Bed Methane

Methane from coalbeds is a rapidly growing source of natural gas and now accounts for about 7% of USA production. The gas is normally produced from shallow wells and is quite lean, rarely containing substantial quantities of hydrocarbons heavier then methane. The gas as produced is water saturated and commonly contaminated with carbon dioxide. The level of carbon dioxide varies widely with the source and location. We have commonly seen levels on the 4-5% range in the Powder River Basin, about 12% in the San Juan Basin and much higher levels in deeper (and heavy hydrocarbon containing) formations.

The gas produced at the wellhead is at low pressures and typically routed through a screw compressor to boost the pressure to about 80-120 psig. The gas is then further compressed to high-pressure and processed to pipeline specifications.

Because the pipeline requirement is at high pressure any system to remove the CO2 will operate at elevated pressure. Both amine and membrane systems prefer high pressures of 800+ psi. The Molecular Gate operating system pressure is flexible (80 – 600 psig) but in most cases prefers a lower pressure at the discharge of a booster screw machine running at 100-200 psig. The choice of the design pressure is project specific for any CO2 removal technology.

A typical arrangement for the Molecular Gas System for coal bed methane is shown in Figure 4.

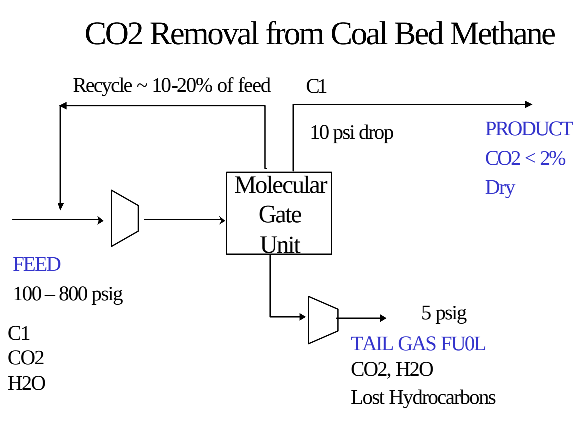


**Figure 4 – Typical Coal Bed Methane Process Flow Schematic**

It is common for coal bed methane to contain carbon dioxide and many amine-based systems are used for the removal of this impurity. In addition to the usual operating challenges of these amine systems, coal bed methane is generally H2S free and corrosion concerns can require consideration.

A glycol dehydration unit to remove water and meet the pipeline specification typically follows the amine system (while not being required by the Molecular Gate system).

In the Molecular Gate system carbon steel construction is used and, since it is a dry system, corrosion is not a concern. Since the tail gas from the vacuum pump contains water and carbon dioxide, attention to corrosion is required there and prevention of liquid water carryover into the gas engine fuel is required.

In addition to the removal of carbon dioxide the system also dehydrates the feed stream and a water free pipeline gas product is produced in a single step.

Carbon dioxide is removed by the system to low levels, typically 2 percent, and lower levels are achievable. Most market interest is to meet the pipeline specification of 1.5 – 3.0% and maximizing the level of carbon dioxide in the product provides the lowest cost and highest methane recovery design. The product purity is flexible and lower levels can be achieved through a simple change in the adsorption time. These low levels include the ppm levels required for LNG pretreatment.

To maximize the methane recovery rate a low-pressure recycle stream is extracted during the process cycle and recycled back to the main feed compressor. This process step requires an incrementally larger feed compressor. It permits high methane recovery rates, typically ninety-five percent, to be achieved by the Molecular Gate system.

## Process Optimization

Because the system does not recover all the methane and loses a portion into the tail gas, use of the tail gas is a process optimization for each project. Where the coal bed methane feed gas contains less than about 8 percent carbon dioxide, the tail gas from the system has a sufficient heating value to provide fuel to the feed compressor. This is an important consideration. Since the main feed compressor will typically consume about five percent of the available feed, a Molecular Gate PSA unit operating at ninety-five percent recovery of methane allows the resulting tail gas to be in balance with the fuel demands of the main feed compressor. In this manner, there is essentially no loss of methane from the system. The design of the fuel supply to the gas-engine is an important consideration and is evaluated on a case-by-case basis with gas engine suppliers.

Where the coal bed methane contains higher levels of carbon dioxide, the tail gas fuel is of low heating value. In this application the system can be configured to split this tail gas into a higher heating value portion suitable for driving the gas engine and a lower heating value component. This design aims to minimize the loss of methane into the low heating value portion of the tail gas. While this solves the need to make use of the tail gas it adds cost. Alternately, depending on the overall fuel demand, a portion of the feed stream (or recycle stream) can be blended with the tail gas to spike the heating value such that it can be used to drive the gas engine.

The level of carbon dioxide in the feed can also vary over time since as the pressure of the wells decreases the carbon dioxide level can increase. Design for a flexible system is required and some increase in capacity is possible through cycling the adsorbent beds more rapidly. If substantial flow rate increases are anticipated the system can be sized to allow the addition of adsorber vessels/adsorbent in the future for debottlenecking purposes. In general such expansions can be accomplished for a fraction of the cost of grass root facilities.

## Example – Coal Bed Methane

In the example in Table 2, Coal Bed Methane with about 6% carbon dioxide requires removal to 2%. In this design the raw feed is 5 MM SCFD and the recycle rate back to the feed compressor is about 0.60 MM SCFD (12%).

| | Design Feed | Design Product | Design Tail Gas |
|---|---|---|---|
| Flow, MM SCFD | 5.00 | 4.62 | 0.38 |
| Pressure, psig | 300 | 290 | 5 |
| Temperature, F | 60-120 | 60-120 | 60-120 |
| Composition, Mol % | | | |
| C1 | 94.00 | 97.70 | 49.23 |
| O2 | 0.05 | 0.05 | 0.03 |
| N2 | 0.24 | 0.25 | 0.13 |
| $CO_2$ | 5.71 | 2.00 | 50.62 |
| $H_2O$ | Saturated | Dry | Balance |

**Table 2 – Example for Coal Bed Methane Material Balance**

Fuel Evaluation:

<u>Fuel Consumption</u>

| | |
|---|---|
| Wellhead Pressure | 17 psia |
| Feed Pressure | 315 psia |
| Feed Compression | ~1000 BHP |
| Fuel Required for Compressor | ~10 MM BTU/hour |

<u>Fuel Availability</u>

| | |
|---|---|
| Tail Gas Heating Value: | ~500 BTU/ft3 |
| Tail Gas Contained Heating Value: | 7.9 MM BTU/hour |

In the above example the fuel demand and contained heat in the tail gas are in near balance. This balance is site dependent, especially with respect to the feed pressure to the CO2 removal system

Some gas engine manufacturers commonly address operating gas engines on low quality fuel. In general a dual fuel carburation system or a fast acting air/fuel ratio controller such that the engine can operate with the normal tail gas as fuel but also operate with the raw feed (or pipeline gas) for start-up or upset conditions.

The vacuum pump on the Molecular Gate tail gas is a single stage system and is chosen between positive displacement blowers, rotary vane machines and liquid ring machines. Such machines are commonly used in coal bed methane production to enhance the gas flow rate from the coal bed and its operation does not present any special challenges. The system is fitted with oxygen sensors and automatic shutdown due to the possibility of air (oxygen) ingress under vacuum conditions.

The vacuum pump is normally electrically driven, though gas drives can also be utilized.

## Oxygen Contaminated Feeds

Oxygen can be present in coalbed methane due to the low-pressure operation. Even where not initially present, oxygen can be introduced when wells are put on vacuum or additional wells are added.

In a Molecular Gate system designed for the removal of carbon dioxide, oxygen will pass through the bed of adsorbent and be present in the methane product stream. Low quantities of oxygen are not generally a concern but the specification on oxygen should be clarified with the pipeline company. In our experience, we have seen a wide range of oxygen specifications from low ppm levels to a few thousand ppm.

In an amine system for coal bed methane oxygen can degrade the solvent and cause corrosion. In membrane systems the oxygen is not generally a concern but will split between the rejected CO2 and the pipeline sales gas product.

Note that Molecular Gate-Nitrogen Rejection systems designed for nitrogen removal will also remove part of the oxygen along with the nitrogen.

## Applications – Natural Gas Upgrading

In most cases where the Molecular Gate system is applied for natural gas upgrading, feed is available at high pressure, and a slightly different flow scheme is applied as shown in Figure 5.

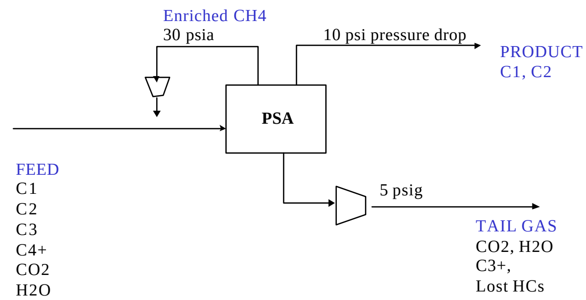


**Figure 5 - Typical block flow diagram for $CO_2$ removal from natural gas**

Making use of the tail gas is the main consideration in applying the system to $CO_2$ removal from natural gas. For a coal bed methane application a use for the tail gas fuel exists in the fuel demand by the main feed compressor. In natural gas applications the recycle compressor has a fuel demand but this is typically about 2% of the available feed, thus under typical recovery rates of 95% excess fuel exists.

This fuel balance is a site specific optimization but one that must be addressed for each project. Where fuel demand is not available we have demonstrated over 99% methane recovery for high performance systems.

Unlike most coal bed methane feeds natural gas also contains at least some level of heavier hydrocarbons. In treating natural gas feeds where heavy hydrocarbons are present, they are partly removed, with the carbon dioxide, through adsorption on the surface of the adsorbent. Where justified by the quantity of the NGL components additional processing can be applied to recover them as a liquid.

## Comparison with Amine and Membrane Technology

Removal of carbon dioxide from natural gas feeds is widely practiced and a variety of amine solvents are commonly applied for its removal. Membrane systems are also attractive for certain applications and becoming more widely accepted by industry. To this range of applications, Molecular Gate fits within certain niches.

Coal bed methane is an ideal application for Molecular Gate systems, since they remove both carbon dioxide and water in a single step. Since feed compression is required there exists a recycle compressor and a home as fuel to the gas engine drive for the methane that is not recovered as sales gas.

The relative cost of the Molecular Gate system, amine system and membrane system are project specific and specific process requirements can be defined in which each of the technologies would be selected. As a general rule the overall costs are roughly similar and operational differences enter the evaluation. In general for low pressure applications the Molecular Gate system can have an advantage, especially where a use for the tail gas fuel exists while high-pressure applications can favor amine or membrane systems. A feed pressure of 100 - 400 psig is about optimum for the Molecular Gate system. In cases where the feed source is at low pressure but the pipeline is at high pressure it may be advantageous to operate the system at a compressor interstage (such as 100 – 400 psig) and to compress the purified product gas.

A higher feed pressure would have a benefit for the amine unit due to higher loading of the carbon dioxide. High feed pressures can also make a membrane unit worthy of consideration. In the same manner as the Molecular Gate system the membrane unit would use the low-pressure carbon dioxide rich permeate stream as fuel to the main feed compressor.

## NGL Recovery

In treating natural gas the removal of heavy hydrocarbons along with the carbon dioxide is an issue that needs to be addressed. These components can be used as fuel along with the rest of the tail gas but this may not always be possible or may result in excess available fuel. The co-removal of heavy hydrocarbons can have an advantage in meeting pipeline dew points but generally would be viewed as a disadvantage with the system penalized by the loss of the heavy components with the carbon dioxide impurity.

The recovery or use as fuel for NGL components is always a consideration for natural gas upgrading and processing for their removal from the feed or Molecular Gate tail gas can be economical.

## Summary

In applications for carbon dioxide removal, Molecular Gate technology offers a new route for meeting the long established needs of the natural gas industry. The successful operation of the first system for carbon dioxide removal at Tidelands Oil Production facility in Long Beach, CA demonstrates the technology.

Subsequently 30 projects are underway with flows from 0.5 MM SCFD to 10 MM SCFD.

The Molecular Gate adsorbents and processes offer new technology for separations beyond those presented in this paper. Development of other separations using Molecular Gate technology is possible as the technology continues to evolve.

## Acknowledgements

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