

MERCURY REMOVAL FROM NATURAL GAS & LIQUID STREAMS

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Introduction

As an element in the periodic table, mercury is found at trace levels in air, sea water and fossil fuels, including natural gas. The presence of mercury in natural gas became a problem after the catastrophic failure of the aluminum heat exchangers at Skikda in 1973 and the discovery of similar damage at the Groningen Field in the Netherlands. In its elemental form, mercury in natural gas amalgamates (forms an alloy) with the aluminum in heat exchangers, eventually causing physical failure. Current industry practice recommends the complete removal of mercury to prevent damage to aluminum heat exchangers.

Mercury has been detected at low trace levels up to 300 micrograms per cubic meter ($\mu\text{g}/\text{Nm}^3$) in natural gas on all five continents and in the Pacific. Typical amounts are usually below 100 micrograms per normal cubic meter ($\mu\text{g}/\text{Nm}^3$). Actual mercury levels analyzed by UOP in natural gas at 13 plant sites in Africa, the Far East and the United States are reported in Table 1. Mercury must be removed below detectable levels, or 0.01 $\mu\text{g}/\text{Nm}^3$ to avoid mercury-caused damage.

These levels of mercury are not an environmental problem. The OSHA mercury limit in air is 50 $\mu\text{g}/\text{Nm}^3$. To get a better understanding of the levels of mercury in natural gas, one of the authors (John Markovs) analyzed his breath and found it to contain about 10 $\mu\text{g}/\text{Nm}^3$ of mercury because of the amalgam fillings in his teeth. This level is comparable to some natural gas streams. The detectable level of mercury in HgSIV purified natural gas is 1/1000 of that amount. Usually, mercury is described in micrograms per cubic meter ($\mu\text{g}/\text{Nm}^3$). One $\mu\text{g}/\text{Nm}^3$ is equal to 0.12 parts per billion by volume (ppbv) or 1.2 parts per billion by weight (ppbw) for natural gas with a molecular weight of 20. Purified natural gas with mercury content below the detectable level of 0.01 $\mu\text{g}/\text{Nm}^3$ corresponds to less than one part per trillion by volume (pptv).

Mercury Analytical

Because mercury is present at such a low level in natural gas and because some mercury is often present in the environment, an accurate analysis of the process stream is difficult. An accurate analysis requires a good analyzer and properly purging sampling points to avoid contamination. A number of analyzers are available that claim capability at the level of parts per trillion by volume. The detection mechanism may involve such means as electron fluorescence, cold vapor atomic absorbance, atomic emissions spectra or electrical resistance. None of these analyzers can directly detect even the parts per billion by volume level of mercury present in typical natural gas, let alone the parts per trillion by volume level in the purified gas. All of them rely on the principle of passing a sample stream through a trap and then desorbing the mercury from the trap as a concentrated pulse into the detector. Some of these traps may consist of silver or gold gauze or gold-coated inert particles such as silica or sand. The desorption is accomplished by applying external heat.

Laboratory studies found that an atomic emissions spectrometer (such as Hewlett Packard Model 5921A) coupled with a good quality gas chromatograph (such as Hewlett Packard Model 58900) provide an accurate way to measure mercury in both gas and liquid samples, as long as proper column technology is used. The electrical

resistance type mercury analyzer manufactured by Arizona Instrument Co. works well for both laboratory studies and field analyses. In this analyzer, one leg of a Wheatstone bridge arrangement is made of gold film. As mercury passes over the film, mercury amalgamates with the gold, changing its resistance.

In practice, mercury is accumulated from the sample stream by passing the stream through a trap containing a gold wire. This mercury trap is called a dosimeter. When sufficient mercury is collected, the trap is connected to the mercury analyzer. Mercury-free air is passed through the trap and into the analyzer. Finally, the gold wire in the trap is electrically energized by heating it instantaneously and desorbing the collected mercury into the wheatstone bridge detector. The analyzer provides a reading corresponding to how much mercury the detector has seen. The maximum that the analyzer can react to is 84.4×10^{-9} g of mercury. Thus, the process stream collection time through the trap needs to be consistent with the expected mercury level.

In doing field measurements, the layout of the sampling system, including the sampling connection on the process line, is important. In a typical process plant, this connection may be a section of 3/4-inch carbon steel pipe 12 to 18 inches long. Even this short section of line can take many days to come to equilibrium with the fluid phase, especially if the mercury content in the process line has gone from a high to a low level. To get a faster response, the sampling connection should be modified as shown in Figure 1. This can be done prior to plant start-up or during any subsequent time when the process line has been depressurized.

UOP's Background in Mercury Removal

UOP's Engineering Products Group developed and commercialized a regenerative process for mercury-removal that used proprietary adsorbents in the early 1970's. The process, PURASIVHg,* removed approximately 100 ppmv mercury from chlorine plant tail gas, which was mostly hydrogen, in a fixed bed thermal swing regeneration adsorption unit.

UOP's Molecular Sieve Department began work on the problem of mercury-removal from natural gas soon after the industry became aware of the problem. The initial result of this work was U.S. patent 4,101,631, which was filed November 3, 1976, and awarded July 18, 1978. This patent describes a product that effectively removes mercury at levels as low as 0.02 ug/Nm³ from natural gas. The product, designated EB-28, consisted of a commercial Type 13X Molecular Sieve loaded with at least 0.5 weight percent (wt%) sulfur. The EB-28 product was more effective for mercury-removal from gas streams than the sulfur loaded on typical commercial activated carbon. Figure 2 shows the performance of EB-28 versus a commercially obtained activated carbon product loaded with 13 wt% sulfur. This performance test on a synthetic gas stream saturated with water at 135F at one atmosphere and containing 2,000 ppbv mercury showed the EB-28 product had a smaller mass transfer zone and achieved a lower mercury content of 0.18 ppbv versus 0.44 ppbv for the carbon products.

Although the EB-28 product provided improved mercury-removal performance compared to other commercial products available, cost-effective mercury removal to below detectable levels required further improvements in product performance. UOP developed and patented the second generation mercury-removal product described in U.S. patent 4,474,896, which was filed March 31, 1983 and awarded October 2, 1984. This product, consisting of Type X or Y molecular sieves with proprietary cations in combination with a polysulfide, provided up to 99% mercury-removal in some tests. The development program, which continued through the mid-1980's, culminated in the commercialization of UOP's* HgSIV* adsorbent in two natural gas processing plants by mid-1988. The HgSIV concept had been identified by early 1987 and, in fact, was disclosed under a secrecy agreement to potential customers in the fourth quarter of 1987.

The HgSIV product can effectively dry and remove mercury at the same time. This dual function is accomplished by coating or loading elemental silver on the outside rim of the

appropriate molecular sieve particle to a depth of about one millimeter. The silver occupies the outside, but no more than 35% of the total molecular sieve particle. Mercury is totally removed on the outside rim of the molecular sieve particle. The interior of the particle is used to remove water. Mercury and water are both regenerated from the HgSIV adsorbent by using conventional natural gas dryer techniques.

Laboratory Studies

The HgSIV adsorbent was tested to determine its effectiveness for removing mercury. A nitrogen stream containing 200 ug/Nm³ of mercury was prepared by mixing in a small stream of mercury saturated nitrogen. This mixture was then passed through a packed bed of HgSIV adsorbent. Mercury levels in the feed and the product gas were determined using the Jerome Model 431 mercury analyzer manufactured by Arizona Instrument Co. Product gas purity of less than 0.0001 ug/Nm³ was demonstrated using the gold wire trap. This accuracy requires ultra-clean sample lines over a long collection period.

The regeneration of the HgSIV adsorbent was studied using the GC-atomic emission spectrometer. The HgSIV adsorbent that had been previously exposed to mercury vapors was placed in the stream going to the detector. A single particle of the adsorbent was used so the detector was not overloaded with mercury. The analytical apparatus had the capability to raise the temperature nearly instantaneously. By using this technique, the required regeneration temperature could be determined.

In the first experiment, the HgSIV adsorbent particle was heated to 300F. This step desorbed some mercury as seen by the detector (Figure 3). After 160 minutes, the temperature was then quickly raised to 608F. This temperature rise produced a large second mercury peak which showed that only part of the mercury had been desorbed at the 300F temperature. A second experiment was then conducted. Here, the mercury-containing HgSIV adsorbent particle was heated to 450F. The resulting

analyzer response is shown in Figure 4. Following the 450F desorption, the temperature was again raised to 608F. However, in this case, no second mercury desorption peak resulted, indicating that the desorption is complete at 450F. Confirmation of complete mercury desorption has been provided by analyzing used HgSIV adsorbent from commercial installations operating at normal dryer regeneration temperatures. Mercury does not accumulate on the HgSIV adsorbent after it has been normally regenerated.

Handling and Disposal of HgSIV Adsorbent

Physically, the HgSIV adsorbent looks and feels just like conventional molecular sieves. It can be in a beaded or in a pelletized form. The HgSIV adsorbent is loaded into an adsorption vessel in exactly the same way as are conventional molecular sieves. For unloading, the same precautions need to be taken as when unloading conventional molecular sieves.

The disposal requirements are also the same as for conventional molecular sieves. Analysis of fresh and used samples of HgSIV adsorbent showed that it passes the EPA TCLP (Toxicity Characteristic Leaching Procedure) test proving that this adsorbent can be safely disposed of by conventional methods.

Commercial Experience

UOP has installed the HgSIV adsorbent in five natural gas dryers and one natural gas liquid dryer through mid-1995. Three additional natural gas and two additional natural gas liquid dryers are scheduled for installation in the first half of 1996. These units are located in the Far East, South America, and the United States. Each of these units is a dryer converted to dual water and mercury-removal by installing a layer of UOP HgSIV adsorbent in the dehydrator vessel. The mercury-removal performance of the first three natural gas dryers and the natural gas liquid dryer is summarized in Tables 2 and 3. Feed gas mercury content ranged from 5 to 50 $\mu\text{g}/\text{Nm}^3$.

Mercury levels in the dried natural gas were below detectable levels of 0.01 ug/Nm³. Each of these existing gas dryers was converted to mercury-removal by installing a layer of UOP HgSIV adsorbent in the dryer vessels without making any equipment or process changes. The liquid petroleum gas dryer was an existing unit converted to drying and mercury-removal by replacing a portion of the drying grade molecular sieve with the UOP HgSIV adsorbent. This conversion was also accomplished without mechanical or process changes. The mercury content of 2 ppbw in the feed liquid was removed to a less than detectable level of below 0.02 ppbw. (In liquid streams, mercury concentration is expressed in parts per billion by weight.)

Regeneration temperature profiles for a natural gas dryer operating with a high feed mercury content of about 40 ug/Nm³ is shown in Figure 5. The mercury desorption profile is similar to a typical water regeneration profile, except that the mercury is completely removed from the HgSIV adsorbent well before the top regeneration temperature is reached. The top mercury regeneration peak concentration could not be measured because it exceeded the capability of the sampling system.

Process Options for Dryer and Mercury-Removal Units

Because the readily available sorption sites are reactivated in each cycle, regenerative mercury-removal with UOP HgSIV adsorbent offers the best protection for downstream aluminum heat exchangers and other process units. The HgSIV adsorbent can be used as a stand-alone unit or in combination with bulk, nonregenerative mercury-removal beds. The latter nonregenerative adsorbent beds are effective for bulk mercury-removal but often fail to provide full mercury-removal. A stand-alone UOP HgSIV adsorbent process is shown in Figure 6. In this process option, a significant portion of mercury removed from the feed stream is condensed in the regeneration knockout and leaves the process as a separate liquid stream.

When an acid gas removal unit is upstream, the plant operator may want to install a nonregenerative bulk Hg removal unit on the plant inlet gas. This unit reduces the mercury in the acid gas streams. The nonregenerative bed can also be used to treat the recycled HgSIV regeneration gas stream. This process option is shown in Figure 7. In this scheme, UOP HgSIV adsorbent is used to reduce the mercury levels from the effluent of the nonregenerative bulk mercury-removal bed to below detectable levels (0.01 ug/Nm³). The nonregenerative bulk mercury-removal bed can be sized to trim high levels of mercury in the feed gas and in the regeneration gas from the HgSIV adsorbent beds to lower mercury levels. Thus, each type of mercury-removal bed is sized for mercury inlet and outlet concentrations at which it operates efficiently. The nonregenerative bulk mercury-removal beds do not have to be sized to attempt to remove all the mercury. Its capacity can be optimized by using the UOP HgSIV adsorbent to remove the lower-range mercury concentrations. Finally, the last fugitive mercury can be removed from the water condensed from the regeneration knockout using a nonregenerative proprietary adsorbent available from UOP. The liquid mercury decanted from the HgSIV adsorbent regeneration knockout is salable.

Mercury Balance in a Gas Plant

UOP has had the opportunity to measure some gas and liquid streams in a natural gas plant. This information suggests that the mercury does not fractionate with the heaviest fractions as would be suggested by the boiling point of mercury. Instead, the mercury concentrates in the liquid petroleum gas (LPG) fraction. Mercury measurements were done in a plant where the feed gas and some liquids feed into the inlet separator at about 680 pounds per square inch gage (psig). The gas was analyzed to contain some 4.1 ppbw of mercury (3.5 ug/Nm³). A sample stream of liquids was flowed into an analytical separator at ambient conditions. The flashed vapors were analyzed and found to contain some 9 ppbw of mercury. The remaining liquids were analyzed to contain 3 ppbw of mercury. Thus, the highest mercury level was in the flashed vapors which were mostly LPG components.

An expected mercury balance in a natural gas plant is shown in Figure 8. In drying and removing mercury from natural gas, little mercury goes with the regenerated and condensed out water. Mercury has very little solubility in water at these conditions. Literature has shown that in an oxygen free environment, the solubility of mercury in water is only about 25 ppbw. As shown in Figure 8, less than 0.5% of the inlet mercury goes with the condensed water. The balance of the mercury leaves with the spent regeneration gas. In this example of drying and purifying 545 MM SCFD of gas containing 2.5 ug/Nm³ of mercury, this level represents only about 34.5 grams of mercury per day. The average concentration of mercury in the spent regeneration gas is about 39.4,ug/Nm³. Often the spent regeneration gas is blended with the plant residue gas into the sales gas stream. This mixing reduces the mercury concentration to that approaching the plant inlet gas.

However, a number of techniques are available to protect the cryogenic portions of the plant, produce mercury-free LPG, and allow no mercury to pass into the fuel system or into the sales gas line. These options incorporate the use of a small bed of nonregenerative mercury-removal adsorbent. One such scheme is shown in Figure 9. Here, the spent regeneration gas, after being cooled and passed through a separator, is sent through a small bed of nonregenerative mercury-removal adsorbent, -such as sulfur-loaded activated carbon. Only a small bed is required for two reasons. The regeneration gas stream is much smaller in volume than the process stream. Also, only bulk removal of mercury is necessary. The mercury concentration does not need to be reduced below that of the feed gas. This means that worrying about containment of the mercury reaction zone in the nonregenerative mercury-removal bed is not necessary. The sorption sites in the nonregenerative mercury-removal adsorbent are completely used. Thus, the nonregenerative adsorbent can be loaded to higher breakthrough loading, minimizing associated replacement expenses.

TABLE 1**Mercury Levels in Natural Gas**

<u>Location</u>	<u>Gas Mercury Level</u> <u>g/m³</u>
Plant 1, USA	5.0
Plant 2, Far East	50
Plant 3, USA	<0.05
Plant 4, USA	13
Plant 5, USA	0.6
Plant 6, USA	8
Plant 7, USA	0.6
Plant 8, USA	2.1
Plant 9, USA	5.5
Plant 10, USA	5.1
Plant 11, USA	120
Plant 12, Africa	<0.05
Plant 13, USA	0.5

Analysis by UOP

TABLE 2**HgSIV Natural Gas Purification**

	<u>Unit A</u>	<u>Unit B</u>	<u>Unit C</u>
Feed Rate, MM SCFD	21	283	250
Temperature, °F	110	64	85
Pressure, psig	1060	600	664
Inlet Impurity			
H ₂ O, lb/MM SCF	7	sat'd	7
Hg, µg/Nm ³	0.8 to 5.0	25 to 50	0.5
Product Gas Purity			
H ₂ O, ppmv	<0.1	<0.1	<0.1
Hg, µg/Nm ³	<0.01	<0.01	<0.01

TABLE 3

HgSIV Natural Gas Liquids Purification

Feed Liquid

Natural gas liquids

MW = 62

20 C

42 barG

H₂O Saturated

Hg 2 ppbw

**(equivalent to 4 $\mu\text{g}/\text{Nm}^3$
in vaporized stream)**

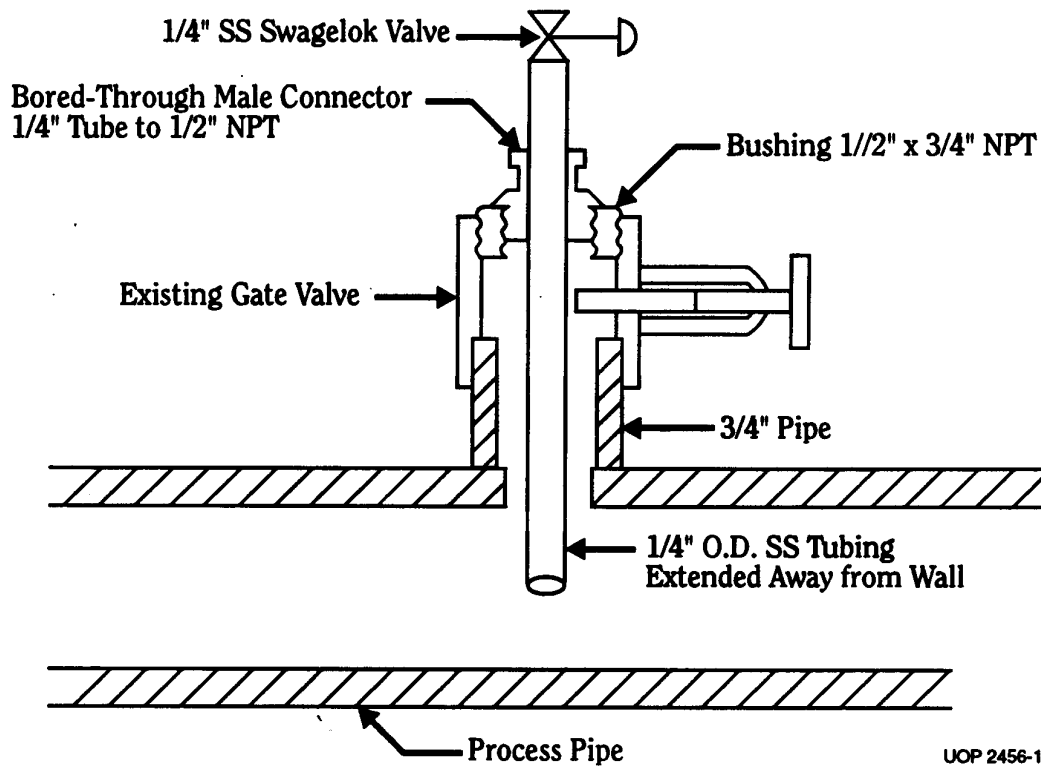
Product Liquid

H₂O less than 1.0 ppmw

Hg Less than 0.02 ppbw

**(equivalent to less than
0.04 $\mu\text{g}/\text{Nm}^3$ in vaporized stream)**

Figure 1
**Sample Point Configuration
for Hg Analysis**



UOP 2456-1

Figure 2
Hg Removal on Sulfur-Loaded Adsorbents

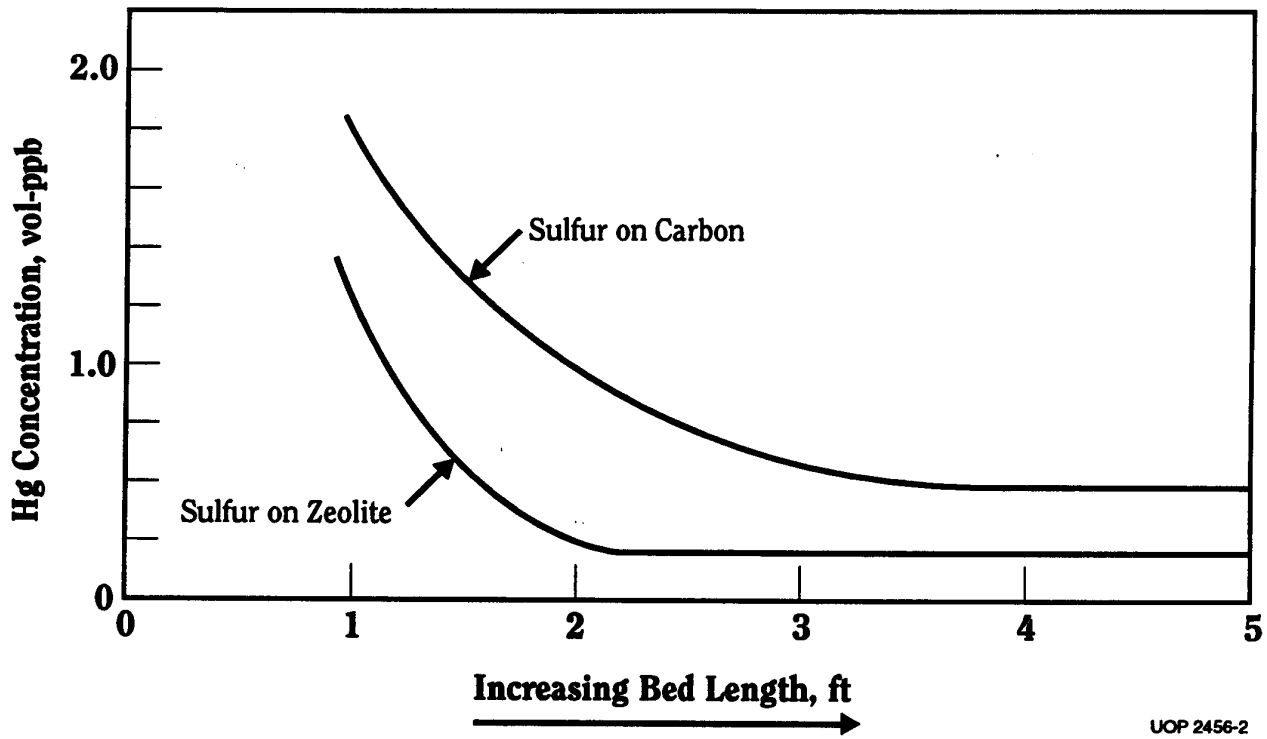
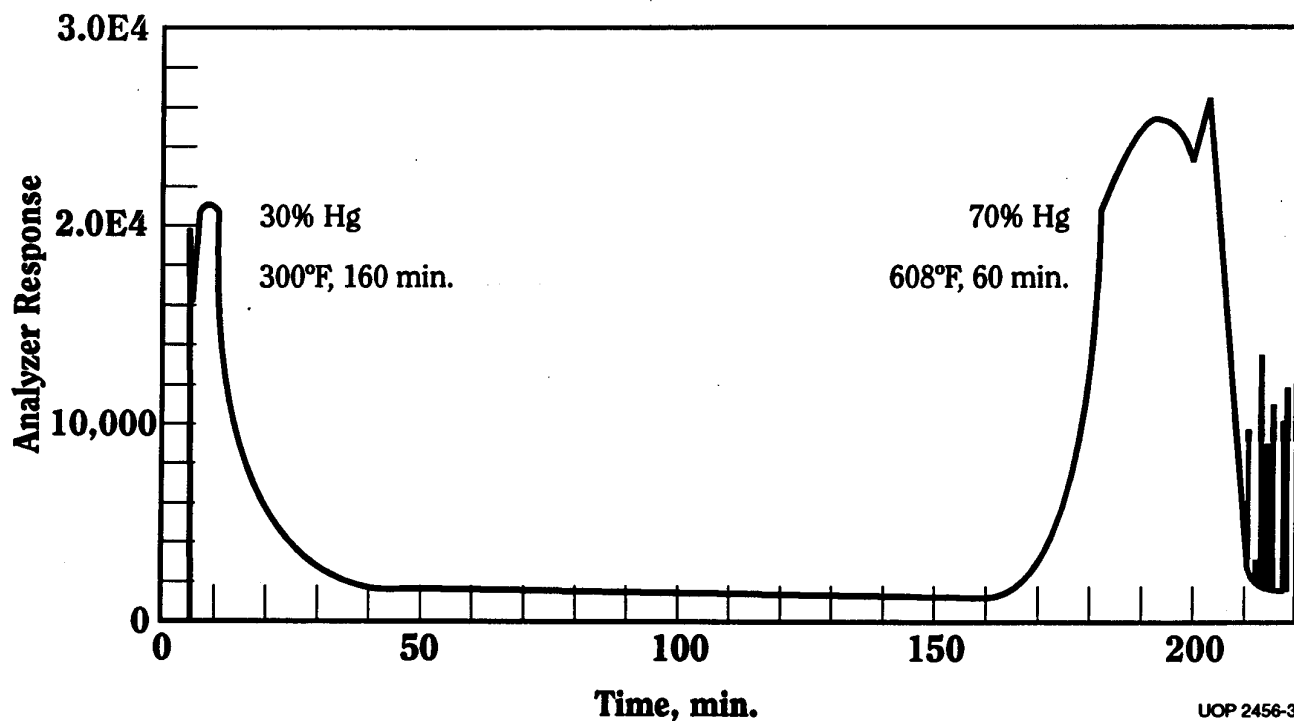
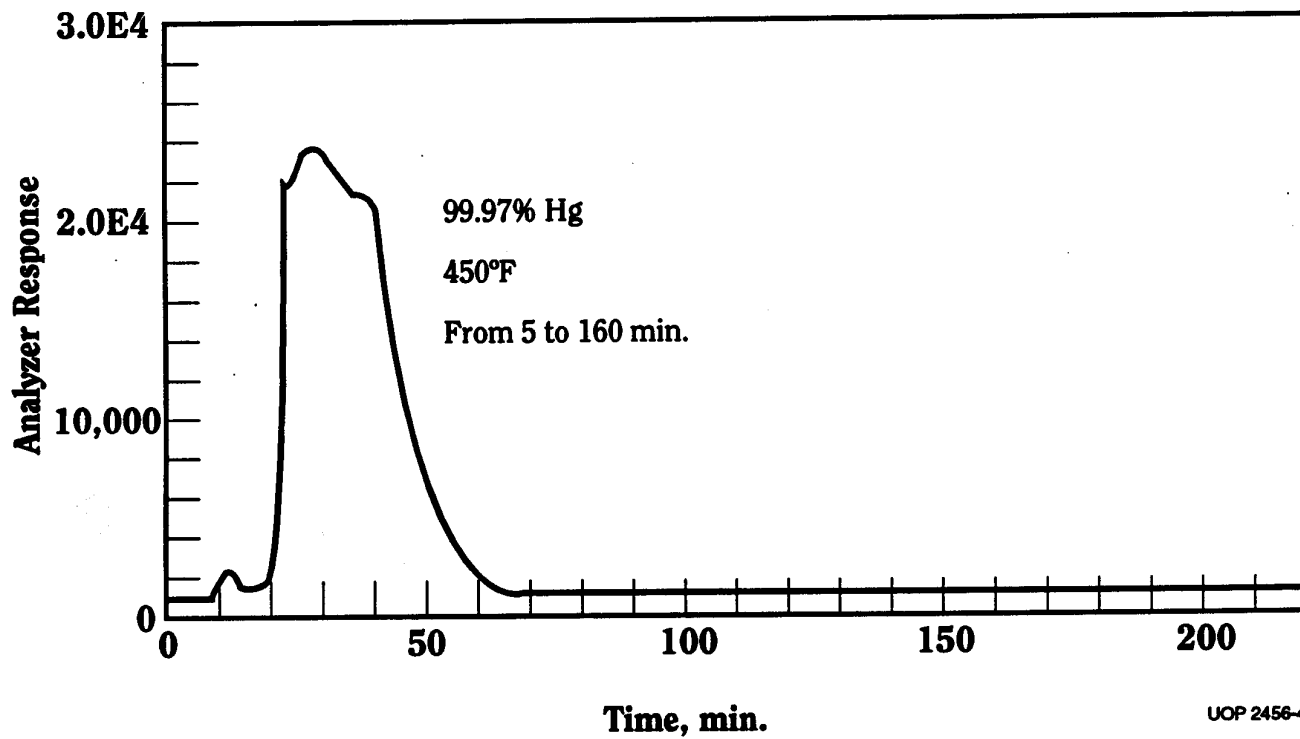


Figure 3
Hg Desorption from HgSIV Adsorbent



UOP 2456-3

Figure 4
Hg Desorption from HgSIV Adsorbent



UOP 2456-4

Figure 5
Hg Desorption Profile
of a Natural Gas Dryer Using
UOP HgSIV Adsorbent

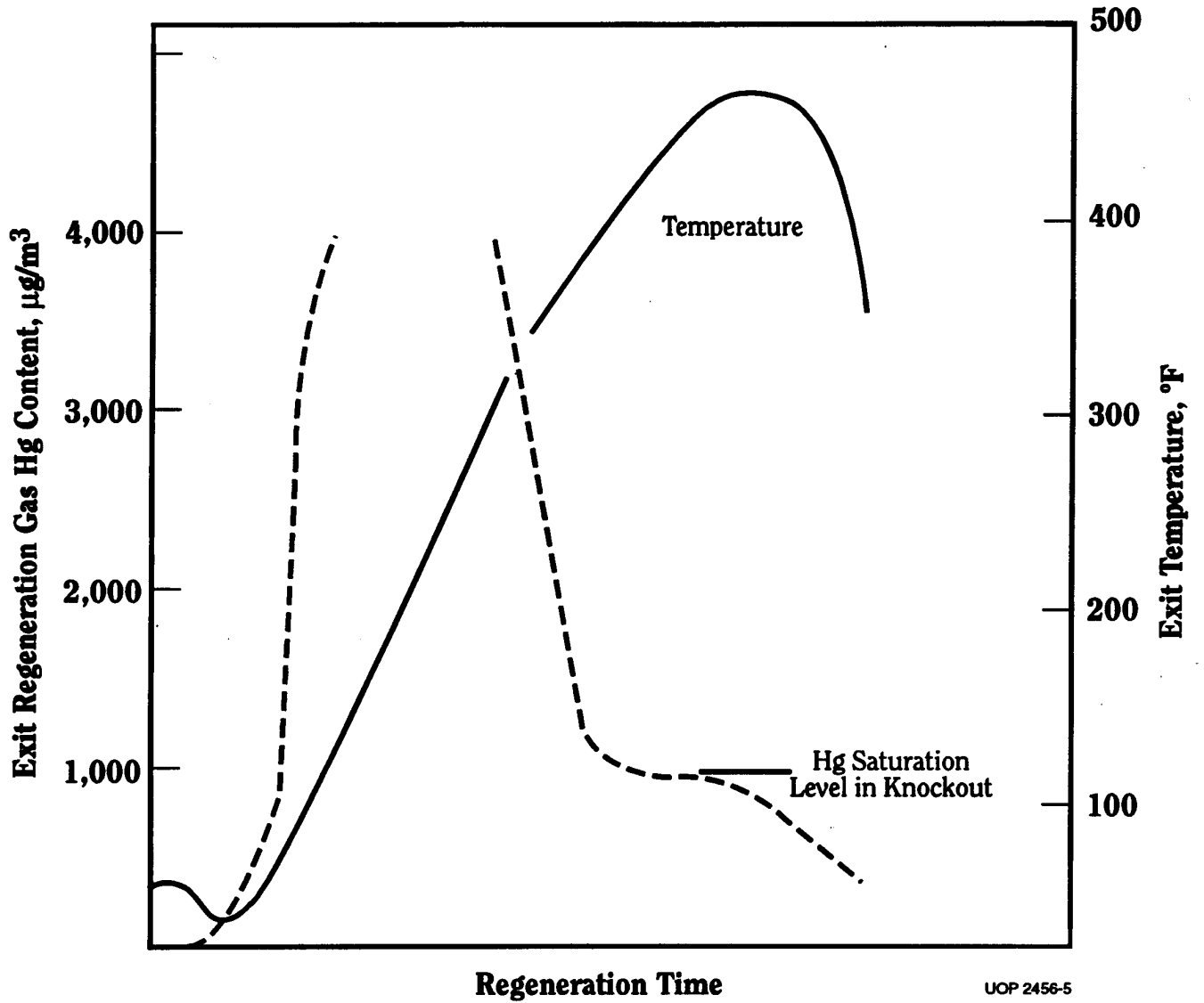
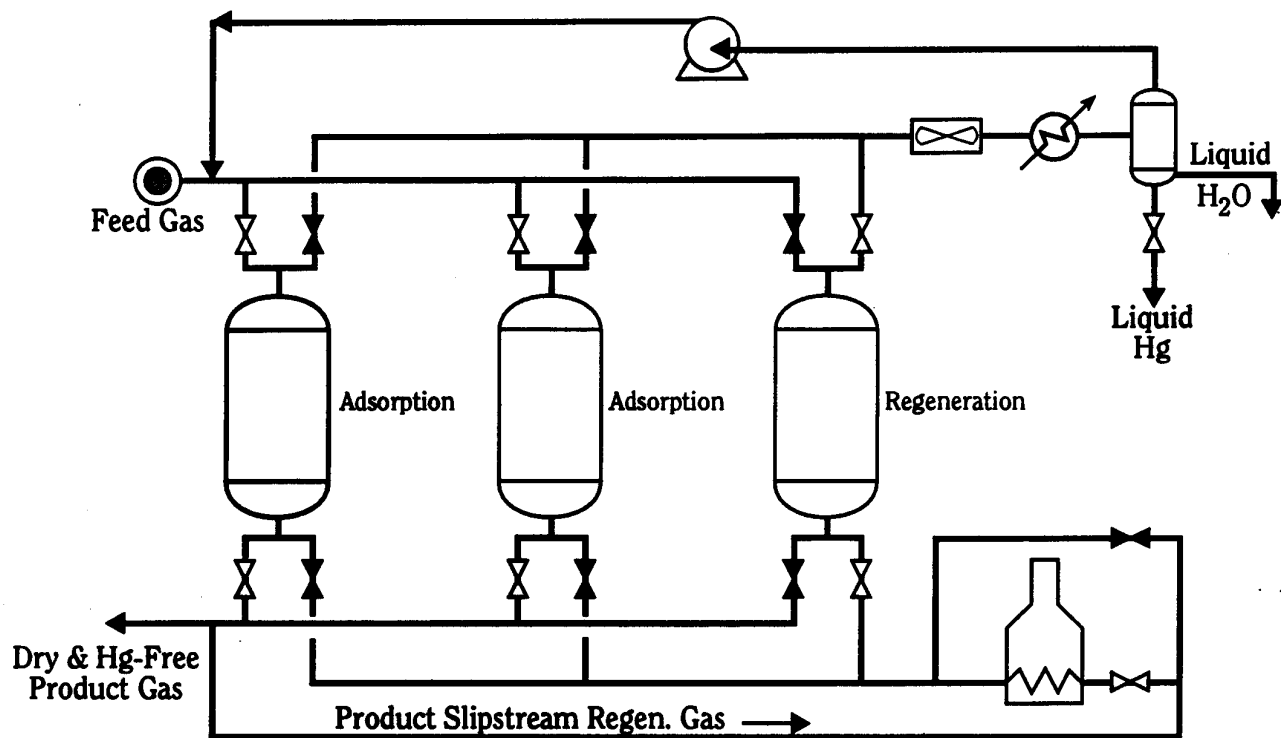
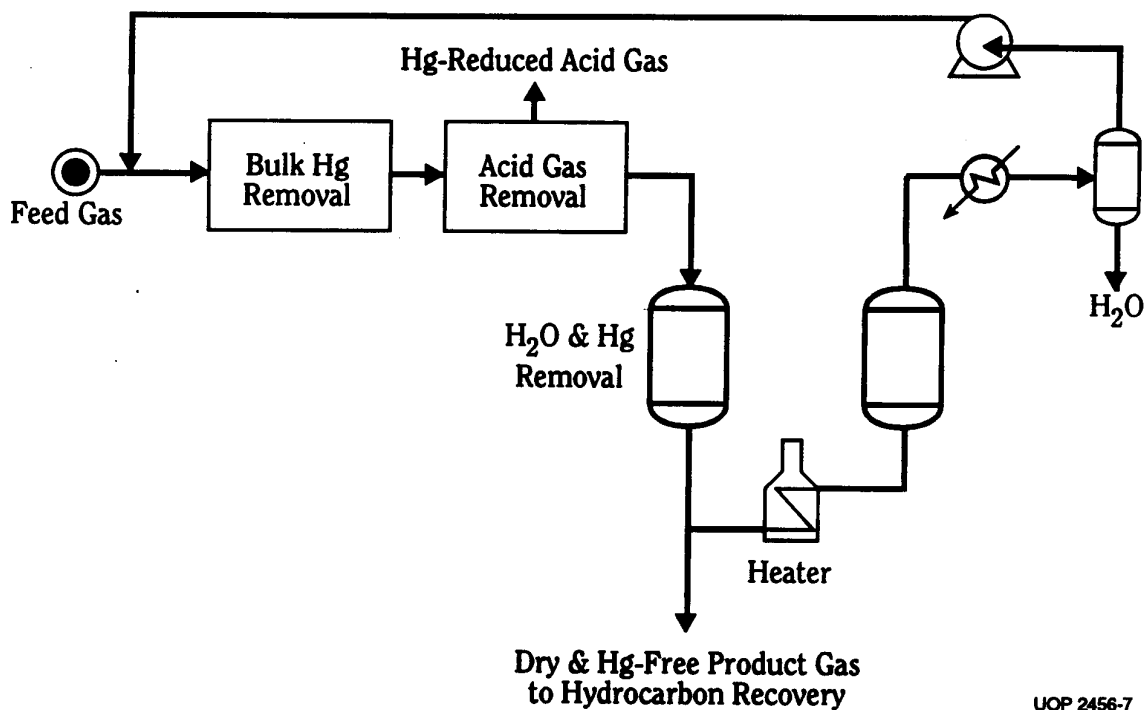


Figure 6
HgSIV Mercury Removal and Recovery System



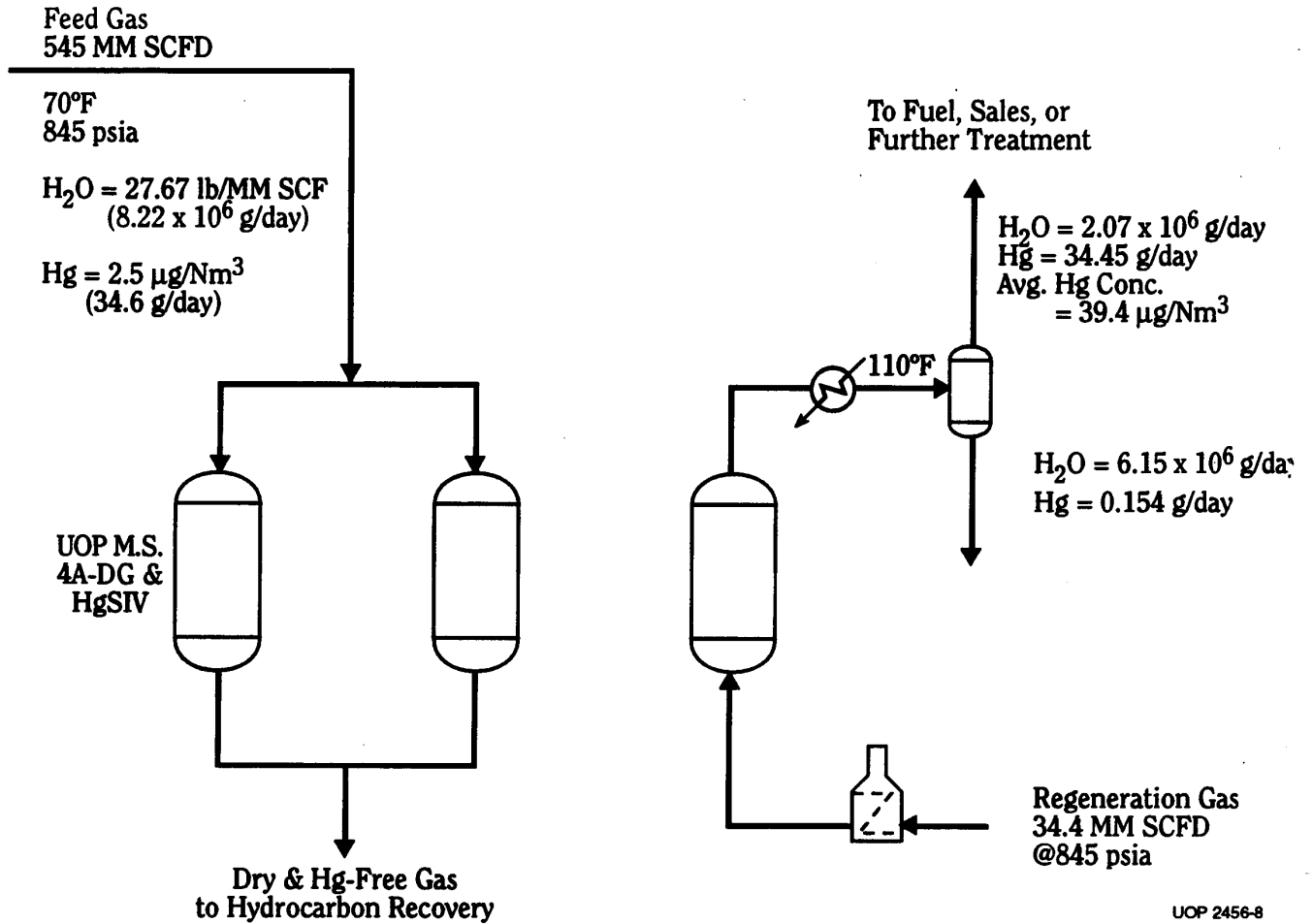
UOP 2456-6

Figure 7
Integrated Hg-Removal System



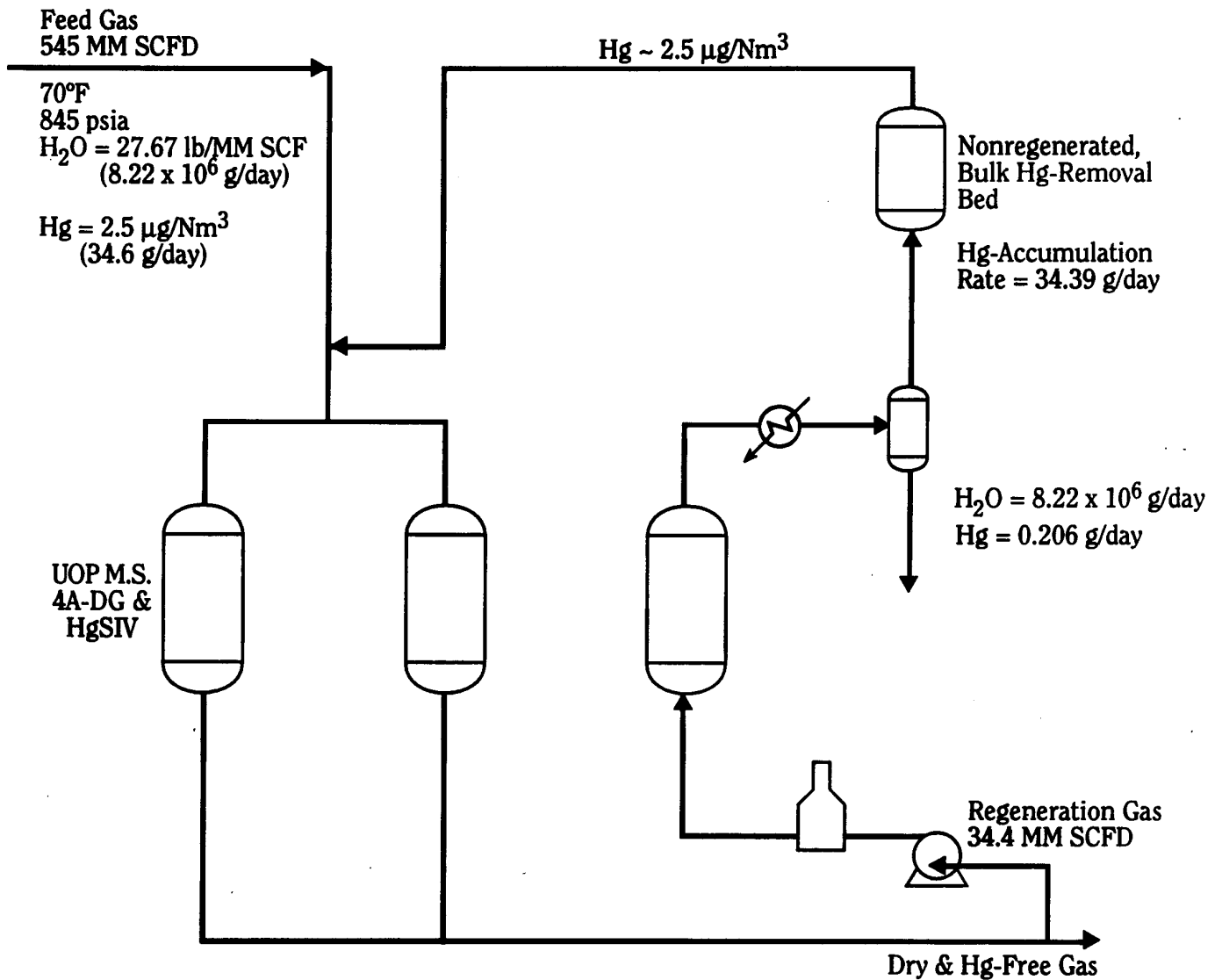
UOP 2456-7

Figure 8
H₂O and Hg Balance
in a Natural Gas Dryer



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Figure 9
Hg Removal with Treatment of the HgSIV Spent Regeneration Gas



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