

Acid gas enrichment part II: maximising selectivity

By recycling about 70% of enriched gas back to the front end of an acid gas enrichment unit, an almost two-fold improvement in SRU feed quality can be enjoyed simply for the minimal cost of providing a recycle line and no increase in operating costs

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Beyond using a common regenerator for the Shell Claus off-gas treating (SCOT) and acid gas enrichment (AGE) units previously described in part I of this two-part article (see *PTQ Gas 2008*), further improvements to the process configuration are possible. The rich solvent from the SCOT unit is always going to be fairly lightly loaded with acid gases. Rather than sending it directly to regeneration, this lightly loaded solvent might be better utilised by sending at least a portion of it to the AGE unit, where it could be used for the bulk removal of H₂S in the lower part of the contactor, and would allow a smaller solvent stream to be sent to the

top of the AGE unit for final gas cleanup. This would result in a reduction in the solvent circulation rate and, therefore, a concomitant reduction in regenerator size and energy consumption, as well as smaller peripheral equipment such as pumps and heat exchangers. This scheme is referred to as the Dual-Solve process by Johnson *et al* (1992), its key feature being the solvent cascade from the SCOT unit, as shown in Figure 1.

The process parameters shown in Figure 2 of the previously published part I of this article and Figure 1 in this article (part II) were kept the same so the effect of cascading could be scrutinised without masking effects from other

parameters having been changed as well. For this example, the solvent flow to the SCOT unit was kept the same as in the original plant, and any solvent flow reductions made possible by the cascading were taken by the AGE absorber. Since only 30% of the total solvent was used by the SCOT column, all of it was subsequently fed to the AGE unit on tray 14 from the top. Simulation using Optimized Gas Treating Inc's proprietary ProTreat software showed that the total solvent circulation rate could be reduced by 20% and the reboiler heat duty by 10%, while maintaining exactly the same H₂S leak values from both the SCOT and AGE

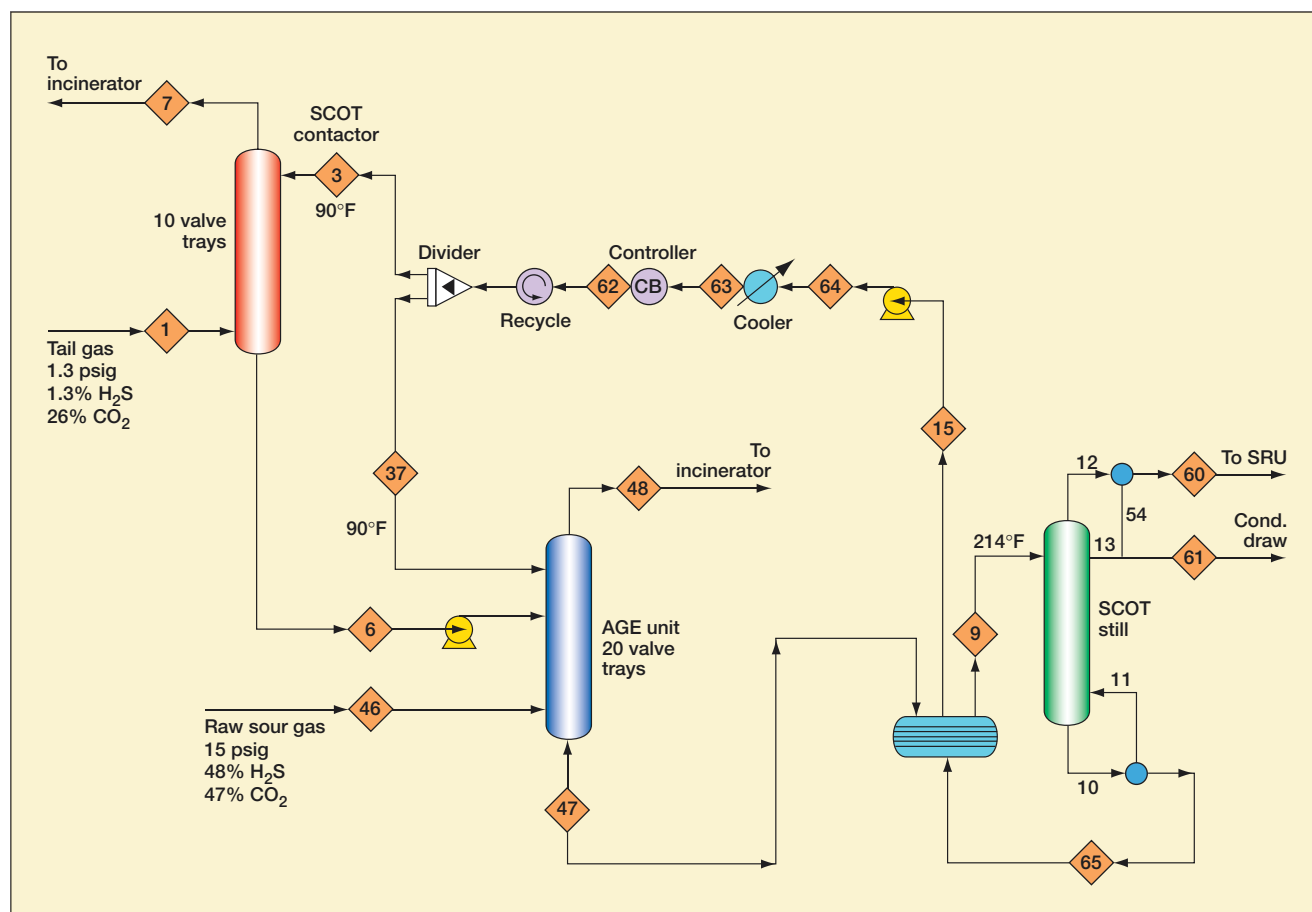


Figure 1 Dual-Solve process

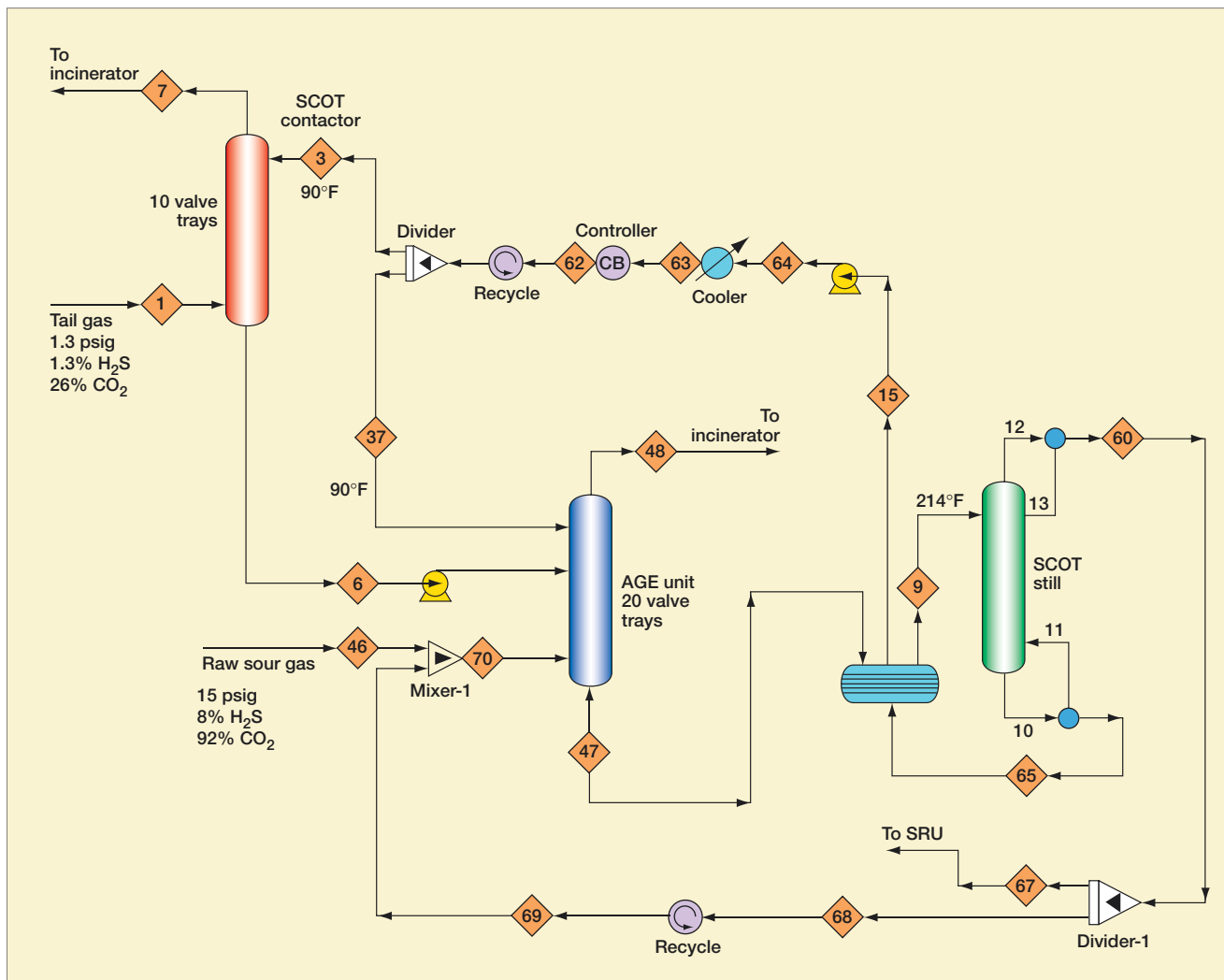


Figure 2 Dual-Solve process combined with acid gas recycle

units. The area of the cross exchanger could be reduced by nearly 40% and additional savings, of course, would be realised in other peripherals as well. But this is not the only scheme that yields benefits.

Enriched gas recycle

The performance of the AGE unit is influenced by the composition of the gas being upgraded, in the sense that the higher the H₂S content of the raw gas, the greater the H₂S content of the sulphur-recovery unit (SRU) feed that can be produced. In the case of Figure 1, for example, the gas to the AGE unit is already quite high in H₂S and the SRU feed produced is even higher still.

Therefore, no further process improvement is warranted in this case. However, for AGE feed gases of much lower quality (eg, 8% H₂S), the scheme in Figure 1 is not the only option.

In the case of a low-quality raw gas, if a portion of the gas produced from the AGE unit's regenerator were recycled back to the AGE contactor feed, the feed stream to the AGE would automatically be richer in H₂S, and you might anticipate that an even richer SRU feed would result. One possible PFD for this scheme is shown in Figure 2. This may or may not require a higher solution rate or a higher regenerator energy consumption, depending on specific conditions. The acid gas recycle

approach could be what is referred to as a "special design feature" by Johnson and Wissbaum (1998) or the proprietary Super Enrichment process by Johnson *et al* (1992), although the literature does not really make this connection clearly. To illustrate the possible benefits of recycle, a lower quality sour gas, 8% H₂S, is used for enrichment. The data shown in Figure 2 are simulated and compared with the same gases processed via Dual-Solve alone. All flows, temperatures, pressures, heat duties and vessel internals were maintained exactly the same between the recycle and proprietary Dual Flow configurations, and the percentage of SRU gross feed returned to the AGE column was varied from 0–75% to ascertain what effect recycle had on SRU feed quality as well as on the leak rates from the two absorbers. Results are shown in Table 1 and in Figures 3 and 4.

By recycling about 70% of the enriched gas back to the front end of the AGE unit, the simulations as shown in Figure 3 predict that an almost two-fold improvement in SRU feed quality, from 40–70% H₂S, can be enjoyed simply for the cost of providing a recycle line. There is no increase in either solvent

Effect of recycle on enrichment and H₂S leak from absorbers

% recycle	AGE H ₂ S leak, ppmv	SCOT H ₂ S leak, ppmv	% H ₂ S in dry SRU feed
0	63	268	40.1
20	76	289	45.4
40	90	313	52.4
60	109	346	62.5
70	138	368	70.7
75	5400	379	76.2

Table 1

rate or regenerator heat duty required in this case. But you come hard up against a limit at around 71% recycle — H₂S breaks through the AGE and the H₂S leak begins to increase dramatically because the solvent rate is just not sufficient to absorb any more H₂S. The contactor gradually goes from lean-end to rich-end pinched as the gas recycle (ie, the H₂S load) increases, until suddenly H₂S breaks through. Undoubtedly, more vigorous stripping or higher solvent rates could be used to achieve even greater enrichment. However, it is clear that acid gas recycling can be a viable means of greatly enhancing SRU feed quality with only a minimal additional capital investment and no increase in operating costs.

Processing conditions and contactor design

There are several questions that could be asked concerning the effect of process conditions such as operating pressures and temperatures, and types of tower internals on the performance of AGE contactors. Is higher pressure better than lower? Should the lean amine be warm or cool? Are trays superior to packing? How much packing and how many trays are best? And are there really general rules of thumb? To answer some of these questions, two extremes will be considered: upgrading very low H₂S content (3%) sour gases and enriching already high H₂S gases (30%) further using generic MDEA in a standalone absorber.

Low H₂S gas

The base case is a 12-tray contactor with one-pass valve trays and 2.5in weirs enriching 3 MMscfd of 3% H₂S, 97% CO₂ gas at 3 psig and 120°F. The solvent is 100 USgpm of 35 wt% MDEA at 85°F. The regenerator takes 220°F rich amine and processes it across 22 valve trays also with 2.5in weirs and using a reboiler duty of 6.0 MMBtu/hr. For this base case, these conditions correspond to a molar stripping ratio of 4, where the stripping ratio is the ratio of moles water to moles total acid gas in the overhead vapour from the still column. Simulation gives a 4.7 ppmv H₂S leak and 91% CO₂ slip for the base case and a regenerator off-gas containing 25.9 mol% H₂S. This is not a particularly wonderful SRU feed and it probably would benefit from acid gas recycle, although to what extent and at what cost is another story — the purpose of this example is to assess sensitivity to changes in process conditions and alternative tower internals. For the discussion, only a single parameter at a time is varied from this base case. The effect of varying parameters away from the base case is shown in Table 2.

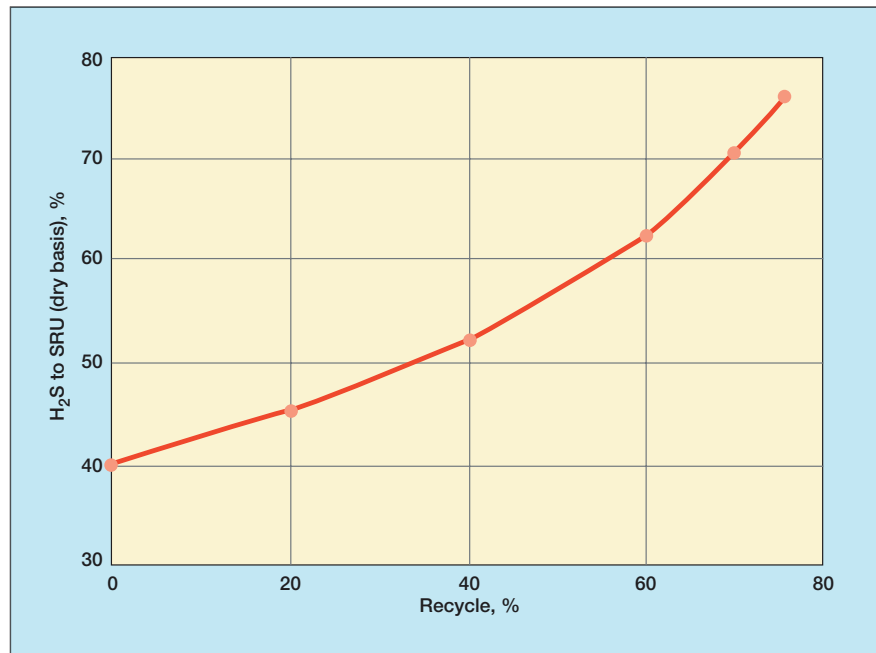


Figure 3 Enriched gas quality

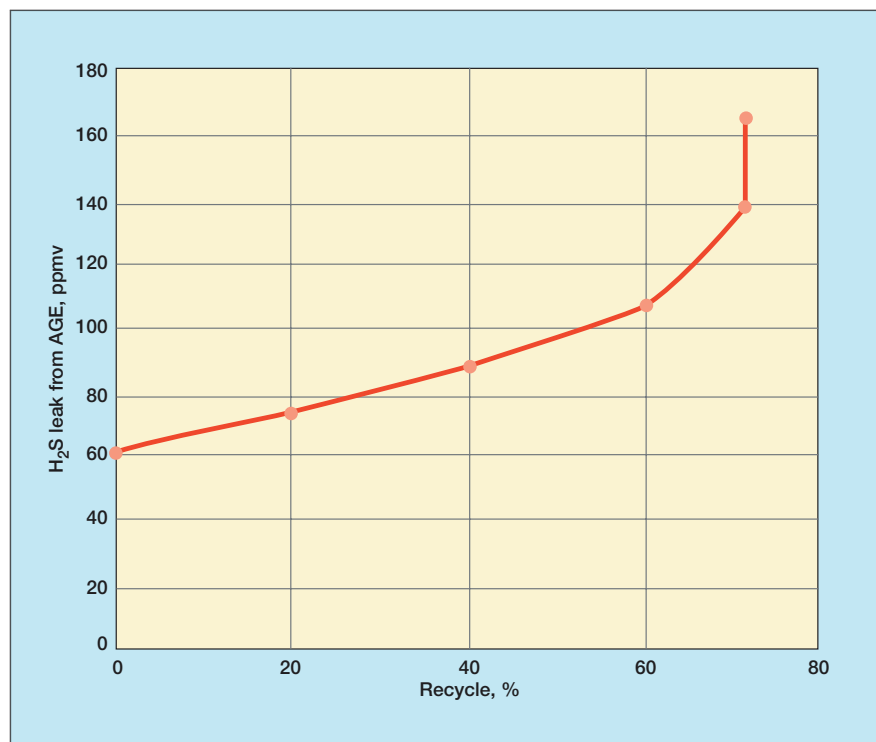


Figure 4 H₂S Leak from AGE unit

Increasing the contactor pressure slightly improves H₂S removal, but at the expense of reduced CO₂ slip and, therefore, a leaner SRU feed gas. There are no surprises from raising and lowering the total tray count: more trays mean better H₂S removal and poorer CO₂ slip and SRU feed quality. However, reducing the tray count can substantially improve the enrichment. The performance of the random and structured packings selected for comparison, however, is somewhat different from the trays, although the differences are not radical.

Assuming that 12 trays on 2ft spacing

can be replaced by 24ft of packing, still with enough headroom for a distributor, the most direct comparisons are between the cases highlighted in bold in the table. The simulation suggests that conventional valve trays in this particular configuration give a few percentage points more CO₂ slip than packing and, therefore, produce a somewhat richer SRU feed.

From a purely mass-transfer standpoint, trays are preferred. However, packings offer small tower diameters (usually not very important at these low pressures) and greatly reduced pressure drops over trays. What emerged from

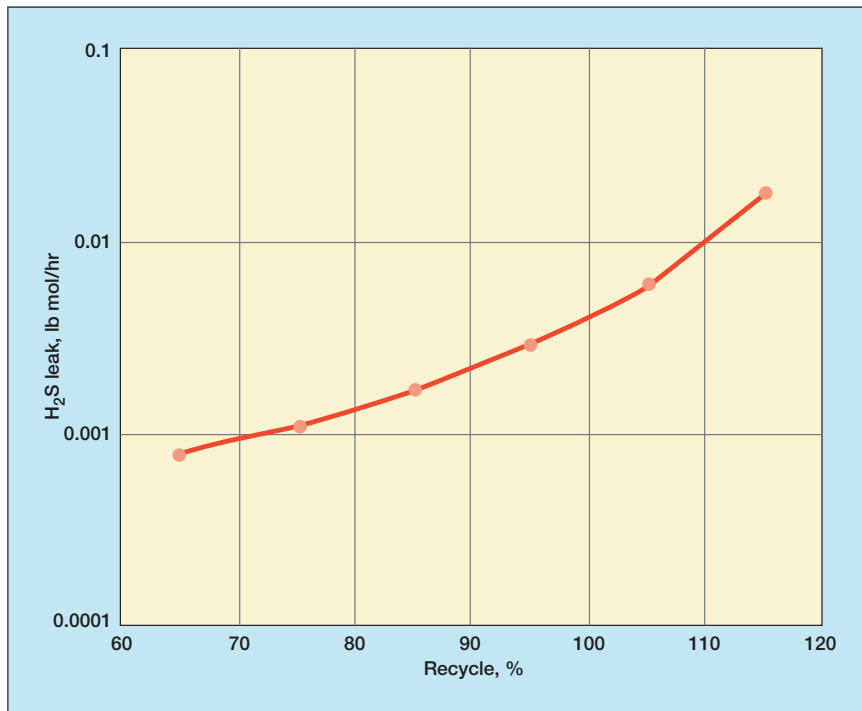


Figure 5 Effect of treating temperature on H₂S leak rate for a low H₂S raw gas

Effect of varying contactor away from base case — low H₂S feed

Contactor condition	H ₂ S leak, ppmv	CO ₂ slip, %	% H ₂ S in SRU feed
Base case (12 trays)	6	91	26
Pressure = 15 psig	2	86	18
20 trays	1	87	19
15 trays	2	90	23
10 trays	16	92	28
8 trays	61	94	33
7 trays	126	95	36
6 trays	270	95	39
Lean @ 100oF	11	92	28
24ft IMTP 50^a	2	85	17
18ft	7	89	21
12ft	77	93	29
24ft ISP 5TX^b	3	84	16
18ft	10	87	20
12ft	80	91	26

a IMTP 50 is a random packing of roughly 2in nominal size, area = 98 m²/m³

b ISP (Intalox Structured Packing) 5TX is large crimp, 60° crimp angle, area = 88 m²/m³

Table 2

Effect of varying contactor from base case — high H₂S feed

Contactor condition	H ₂ S leak, ppmv	CO ₂ slip, %	% H ₂ S in SRU feed
Base case (13 trays)	93	92	80
Pressure = 15 psig	34	86	70
20 trays	41	88	73
15 trays	56	91	78
13 trays	93	92	80
12 trays	154	92	81
11 trays	298	93	82
10 trays	644	94	83
Lean @ 100°F	69	94	83
26ft IMTP 50	34	91	78
20ft	63	93	82
15ft	606	95	86
26ft ISP 5TX	23	82	64
20ft	31	86	70
15ft	52	89	75

Table 3

further simulation work was that if packing of any kind is to be used, it should be large crimp or large diameter; otherwise, selectivity and SRU feed quality will suffer. The caveat is that the packing must not be too big; for example, in this case using 3in Raschig rings gave a predicted H₂S leak of 25 ppmv. The reason is probably the specific surface area of such large rings — 68 m²/m³ vs 88 m²/m³ for IMTP-50. The optimal tray or packing type and size is obviously quite specific to each application. An interesting aside is to wonder whether trays with large valves might not perform better than ones with small openings, since it is known that froth coarseness (hence interfacial area) is related to valve size. This would provide less contact area per tray, so it might favour CO₂ slip.

There is anecdotal evidence that AGE is less successful in locations such as the Middle East, where ambient (and therefore coolant) temperatures are high, so the effect of the lean-amine temperature on performance is worth considering. The simulated effect on the H₂S leak rate is shown semi-logarithmically in Figure 5. In the simulations, all parameters were held constant, including component flows to the AGE contactor, and the temperature of the raw gas was made equal to the lean amine. Over the temperature range 65–115°F, the H₂S leak rate is predicted to rise 20-fold from 0.0008–0.018 lbmol/hr. The corresponding H₂S concentration range is 3–55 ppmv. The H₂S leak is highly sensitive to treating temperature, although in this case, where the raw gas is dilute in H₂S, the leak is predicted to be always less than 100 ppmv.

High H₂S gas

In the base case operation, the feed gas contains 25 mol% H₂S and is treated with 150 USgpm of 50 wt% MDEA. Otherwise, all other conditions are identical to the low H₂S case. Table 3 shows the sensitivity to various parameters.

For this higher H₂S feed, simulation suggests that when the tray count itself is fairly small (but roughly how most people would expect an AGE contactor to be built), removing a single tray (13 to 12) can double the H₂S leak while providing only a very modest gain in SRU feed gas quality. Increasing solvent circulation to hold the H₂S leak constant may wipe away the gain of fewer trays. This kind of sensitivity is not seen with the low H₂S feed because the original raw gas contains so little H₂S in the first place. Replacing the trayed volume of the absorber with an equal quantity of random or structured packing produces lower simulated H₂S leak, but poorer quality SRU feed because this much packing absorbs more CO₂ — only

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slightly more in the case of IMTP 50, but quite a bit more with the structured packing ISP 5TX. The trays, IMTP and ISP internals are hydraulically at 82%, 52% and 40% of flood respectively in this column.

Figures 6 and 7 show the effect of the AGE unit's operating temperature on H₂S slip; both the slip rate and H₂S concentration in the treated gas going to the incinerator are shown. Note the log scale on the leak rate and %leak axes. When the raw gas is already fairly high in H₂S, the effect of contactor temperature on the leak is much more pronounced. Over the temperature range 65–115°F, the leak rate increases by a factor of 500, as does the leak measured in ppmv. Thus, referring to Figures 5, 6 and 7, significant enrichment with manageable H₂S leak is not too strenuous when the feed gas is fairly dilute. However, to enrich 25% H₂S raw gas at high contactor temperatures may be impossible, at least using a simple, straightforward process strategy.

As a final comment, an impossibly low-quality Claus plant feed (3% H₂S) can be upgraded to 25–30% H₂S in a short column, depending on how much H₂S you are allowed to vent (usually set by environmental authority). Furthermore, a sour gas with 25% H₂S can be upgraded to 80% H₂S, also using a fairly short column with a dozen trays or a few feet of packing. With these two columns, you can then produce 80% H₂S SRU feed from a 3% gas (if the contactor can be operated at low to moderate temperatures). But two contactors are unnecessary — the entire upgrade can be done in a single column by using a scheme with a semi-lean stream! This is a good application for a so-called split flow process, in which the fully stripped solvent from a common regenerator's reboiler is sent to the top of the contactor, while a partially stripped (semi-lean) solvent is removed from a midpoint in the regenerator and sent to an intermediate feed point part way down the absorber. This flowsheet is frequently seen in DEA and HotPot processes — perhaps super enrichment of very low-quality gas is another application of the split flow configuration, albeit a more unusual one.

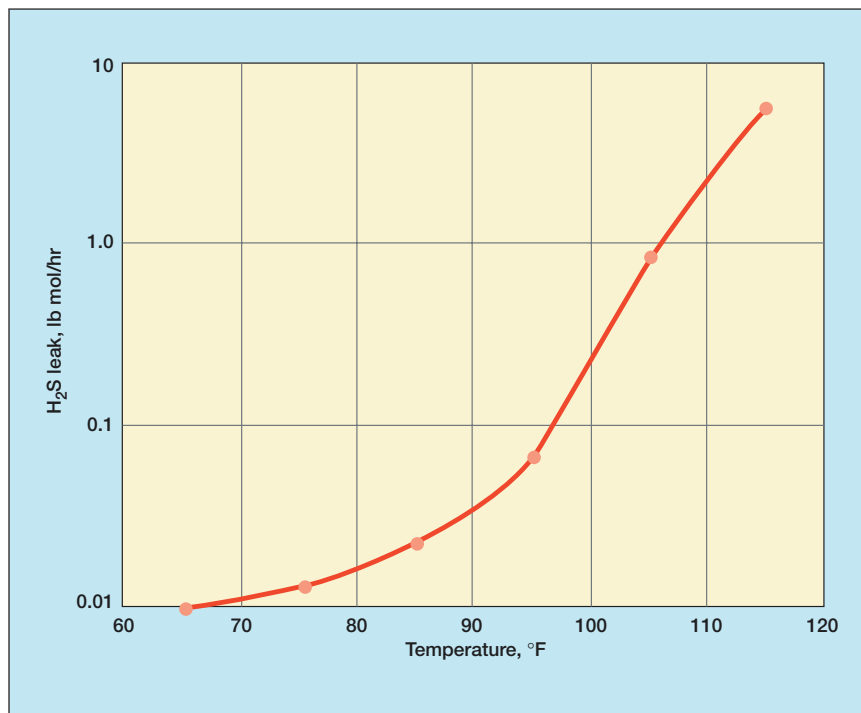


Figure 6 H₂S leak rate (lbmol/hr)

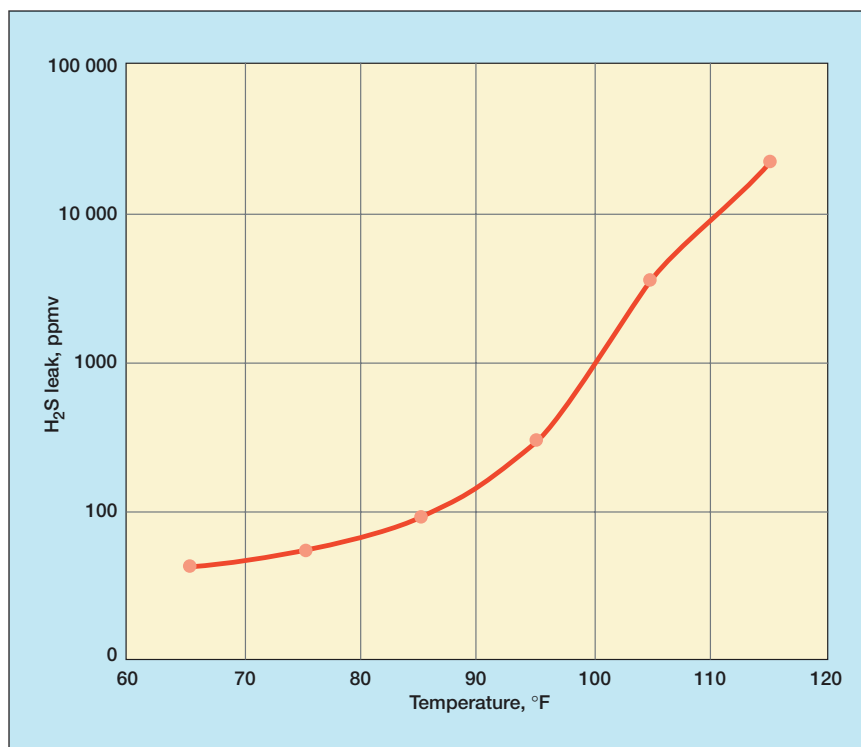


Figure 7 H₂S in gas to incinerator

Offgas enrichment

This example is taken from the paper by Miller *et al* (2001), dealing with the enrichment of the offgas generated by the GTU at the Aquila Navasota Gas Plant in Grimes County, Texas, USA. The raw gas to this plant was 6.5% CO₂ and 25 ppmv H₂S. The regenerator offgas from the GTU flowed nominally at 5.5 MMscfd and was an extremely lean AGE feed gas at 8–10 psig; it contained only 800 ppmv H₂S, with the balance wet CO₂. This obviously presented operations with a real problem

because the H₂S simply had to be removed to meet sulphur emission limits, and the method in use at the time was proving to be very expensive. The paper provides a lucid description of various options, along with details of the amine-based solution selected. Fortunately, the paper also gives sufficient equipment and process information for process modelling, allowing direct comparison between the purely predictive ProTreat simulation and measured plant performance data.

Table 4 compares key plant operating

Operating data and ProTreat simulation compared

	Design	2/11/99	28/11/99	2/1/00	25/1/00
Lean amine to absorber, °F	100	101	98	100	88
Circulation rate, USgpm	40	37.5	33	34	34 (?)
Sour gas rate, MMscfd	5.5	4.59	4.38	4.83	5.1
Treated gas H₂S leak, ppmv	166	144	169	170	130
ProTreat simulated H₂S leak, ppmv	151	132	158	171	148
Simulated enriched gas, %H ₂ S	2.6	2.3	2.2	2.4	2.2

Table 4

and performance data with simulated performance. In the simulation, it had to be assumed that the reboiler duty was as stated in the design, because no measured reboiler data were given for the individual tests. Where amine strength was not reported, 45 wt% (the design value) was assumed. The circulation rate on 25/1/00 was unstated and was taken to be the same as on 2/1/00, the date of the previous performance test.

The simulated H₂S leak is in every case within 10 or 15 ppmv of the reported leak, the only real performance metric reported. Given that the simulations were run using the reported operating data directly without the slightest adjustment or tweaking of any kind, the performance predictions are remarkably close to reality.

The offgas from the regenerator is not exactly rich in terms of a potential Claus plant feed. However, it has already been shown that such a gas can readily be upgraded further to 25% H₂S and from there to 75% or 80% just by using additional short beds of packing or a handful of trays. A process strategy with a single regenerator and two partially and one fully regenerated solvent stream (ie, three solvent streams from the single regenerator) might be a neat solution.

Summary

Acid gas enrichment is an extreme example of applying maximum selectivity to achieve process goals. It is also a supreme test of any simulator's ability not just to model selective treating processes, but actually to predict their performance without recourse even to thinking about adjustable parameters such as tray efficiencies, HETP values, residence times, and the like. The predictions are made not on the basis of experience with similar processes, plants or columns, but on the basis of fundamental knowledge and models of how trays and packings actually perform as mass-transfer devices. Such knowledge, built into the simulator, provides the ability to select the right number and type of trays, and the right amount of packing of the correct type and size to meet specific objectives.

Each of the three operating cases presented here (two using trays and one

using packing) shows that mass-transfer-rate-based simulation is capable of predicting real-world performance even of such a difficult process as AGE. Unfortunately, plant performance tests of AGE operations usually do not measure the H₂S content of the SRU feed, probably because of the hazards associated with handling high (and low) H₂S-content gases. As far as CO₂ slip from the AGE contactor itself is concerned, it would be wonderful to have such data, but it is next to impossible to measure reliably, unless the treated gas rate from the contactor can be measured accurately.

The work reported here indicates that from a selectivity standpoint, trays might be slightly preferable to random packing, and random packing is slightly preferable to structured packing. However, this comment must be tempered by (a) the very slightness of the preference, (b) the fact that when the tower height occupied by trays is replaced by the same height of packing, the packing is a more efficient mass-transfer internal, and (c) the fact that the performance of each and every packing (and tray), whether random or structured, will be different from all others. Therefore, in designing an AGE process, great care must be taken in deciding between trays and packing if mass transfer is the only basis. In situations in which for one reason or another packing is preferred, further judgement must be exercised to ensure the best packing is selected. A simulator that distinguishes between packings based on their mass-transfer characteristics as well as their hydraulics

“A simulator that distinguishes between packings based on their mass-transfer characteristics as well as their hydraulics is an essential tool in reliable design and troubleshooting”

is an essential tool in reliable design and troubleshooting. Similar comments apply to trays, insofar as their mass-transfer performance (especially the all-critical selectivity) depends on the tray vendor and mechanical details such as type of openings, number of passes and weir heights, as well as on approach to flood and hydraulic operating parameters.

Finally, this study indicates that there are no forbidden regions of operation for AGE plants except to say that the production of a super-enriched Claus feed will be extremely difficult, perhaps impossible, if lean amine temperatures cannot be kept below about 100°F. Use of a stripping promoter might extend this temperature upwards a little. Ultimately, it is really a matter of being able reliably and accurately to assess whether one option or another will give satisfactory performance from both technical and economic standpoints, and then to keep the AGE unit running properly by being able to respond sensibly to inevitable process upsets, and changes in feed and ambient conditions.

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