

Acid gas enrichment I: Maximizing selectivity

Understanding AGE operation by examining effects of sour gas composition and solvent strength, including amine partial acidification, operating temperatures, type and total quantity of internals on residual H₂S leak and Claus feed or reinjection gas quality

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Acid gas enrichment (AGE) is a group of methods used to upgrade low-quality off-gas from treating units to higher-quality Claus plant feed or to a smaller volume stream suitable for reinjection. The process objective is to maximise CO₂ slip and minimise the H₂S leak into vent gas from the system, thereby producing a gas enriched in H₂S to the greatest extent possible.

The most common method to enrich is by using a separate absorber for treating the low-grade acid gas stream coming from the regenerator. Because such streams contain very little else besides acid gases and water, virtually the entire sour gas stream can be very readily absorbed if presented with enough solvent. This makes this type of AGE unit a quite severe test of one's ability to model selectivity. Gas flow and composition vary rapidly through the contactor, and concentration profiles can become inverted, forming an H₂S bubble within the contactor.

Another way to enrich the acid gas stream is simply to recycle a (substantial) part of the separated acid gas back into the feed to the contactor. This lets the absorber feed on an effectively richer sour gas and thereby produce a richer acid gas product stream. Almost nothing is free, however, and the cost may be higher solvent circulation and/or increased reboiler energy consumption.

AGE general objective

The last 15 years have seen increased interest in acid gas enrichment (AGE) to provide higher H₂S-content gas to Claus plants, and occasionally for down-well reinjection. The overwhelming majority of AGE plants have a dedicated enriching absorber. Today, the number of these plants operating globally is probably fewer than 25. There might have been more but several have failed to perform as expected and have been shut down, either because gas composition moved into an uneconomic operating region or expectations were unrealistic in the first place. Designing and operating

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AGE plants is a tricky business and requires a different mind-set from conventional high-pressure gas treating plants. Indeed, there is an operating window outside of which AGE is unlikely to give satisfactory results at all, because high enough selectivity cannot be achieved in a single conventionally operated column, or H₂S leak is unacceptably high.

The general objective of AGE is the economic production of a high-quality Claus plant feed from one of lower quality. Process goals are to reach the highest achievable CO₂ slip to produce maximum enrichment, and to keep the H₂S leak in the reject gas as low as possible so that the operation contributes minimally to the plant's total sulphur emission. In other words, high selectivity, and concomitantly, very low H₂S leak.

Designing and operating AGE plants is highly sensitive to a number of parameters, including lean solvent temperature (a serious constraint in the Middle East, for example), feed gas H₂S-to-CO₂ (H₂S:CO₂) ratio, choice of tower internals type, number of contact trays, and solvent selection. Indeed, just getting the tower internals right can play a decisive role in the success of an AGE application.

Part I of this discussion addresses which performance expectations are

reasonable for 'conventional' AGE by examining in detail the effect of sour gas composition, level of solvent regeneration, solvent mix including amine partial acidification, operating temperatures, type of internals (trays, type/size of random packing, type/size of structured packing), and the total quantity of internals (tray count, packed depths) on residual H₂S leak and Claus feed or reinjection gas quality.

Why acid gas enrichment

In the context of sulphur recovery, the primary purpose of AGE is to present the SRU with a high H₂S concentration acid gas feed. High H₂S feed concentrations are beneficial to the SRU for several reasons and, additionally, they benefit the tail-gas cleanup unit (TGCU). First, in the Claus furnace, the acid gas flame becomes unstable below about 45% H₂S in the gas (Johnson et al., 1992). Even at concentrations below 55% H₂S, controls become more complex, and below 35-45% complexities are even greater (Johnson and Wissbaum, 1998). The other side of the SRU coin is to keep the CO₂ concentration low in and of itself, so as to minimise the reaction of CO₂ with H₂S to form COS in the reaction furnace. Eliminating CO₂ from the system hydraulically unloads the entire SRU/TGCU train. A third benefit is the virtual elimination of heavy hydrocarbons (HHCs) and BTEX components from the SRU feed, because the AGE absorber will slip most of the HCCs and BTEX components that reach it in the acid gas from the primary treating plant. Unfortunately, COS and mercaptans are not very soluble or reactive in amines, especially the MDEA-based formulations needed for selective treating. Consequently, these trace sulphur species mainly slip through the AGE absorber and will contribute to the plant's total sulphur emission. In addition, of course, the AGE absorber cannot remove all the H₂S – there will inevitably be a small

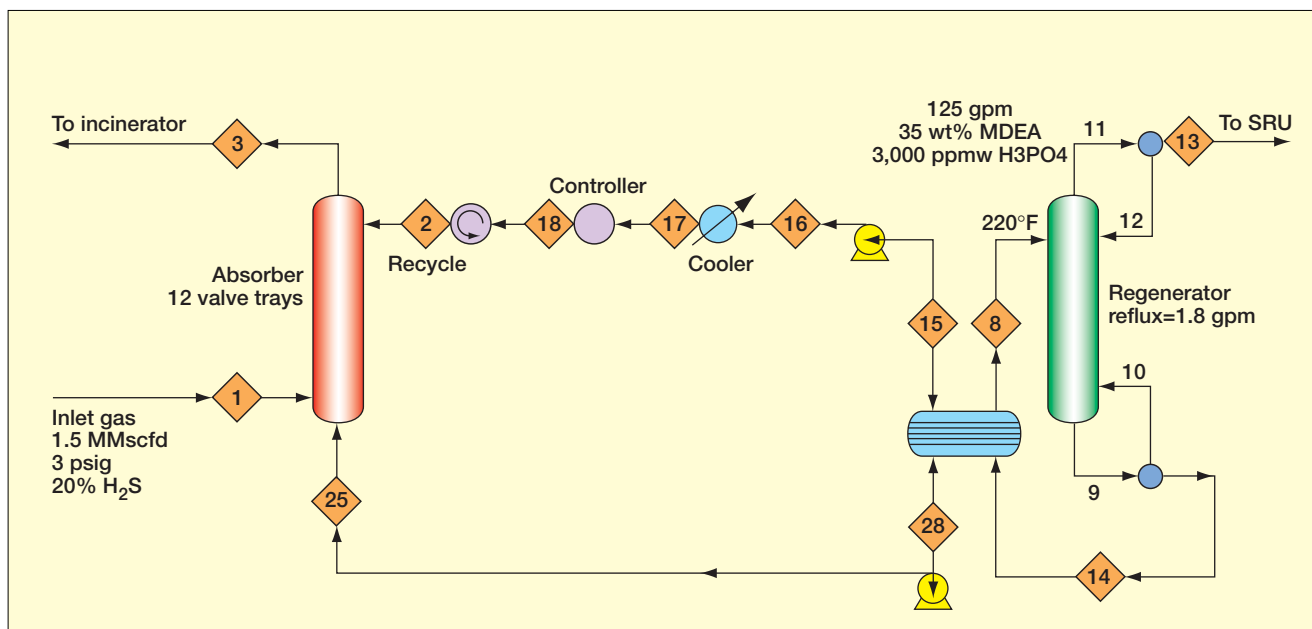


Figure 1 Simple standalone AGE

H_2S leak, a typical leak with MDEA being 100-200 ppmv. However, with certain speciality solvents or by using a stripping promoter such as a few 1000 ppmw phosphoric acid (0.1% to 2 wt% was reported by Kohl and Nielsen [1997] after Dibble [1985]), sulphate ion, or other so-called heat stable salt, an H_2S leak of less than 10 ppmv can be achieved in a properly designed treating plant.

If the acid gas to the SRU is already above 55% H_2S , there is probably insufficient benefit in taking special pains to enrich it further, unless ammonia is also being processed in the sulphur plant, or the plant requires debottlenecking. But in plants treating wellhead gas with a high $CO_2:H_2S$ ratio, adequate CO_2 slip, even using the most selective solvent, cannot produce an SRU feed of sufficient quality. For example, a high-pressure gas containing one or two percent CO_2 and a few 100s of ppmv H_2S cannot be treated with amines to produce an acid gas stream with more than a few mol% H_2S , hopelessly inadequate for a conventional Claus SRU. An acid gas containing 25% H_2S can be processed in an SRU, albeit with some difficulty – a gas with only a few percent H_2S cannot. So AGE is most beneficial when the H_2S concentration is below perhaps 25% in the acid gas from the gas treating unit's regenerator. Even in plants with a moderate $CO_2:H_2S$ ratio of say 4:1, if the plant is nonselective (LNG for example), total removal of acid gas will produce an acid gas stream containing only 20% H_2S . Again, AGE becomes an interesting possibility.

General considerations

AGE is all about selectivity. Obviously, the ideal or perfect process removes all

the H_2S and none of the CO_2 from the raw gas because then solvent regeneration produces an acid gas consisting entirely of wet H_2S – perfect selectivity. Detailed discussions of selectivity have been presented in many places including Anderson et al. (1992) and Weiland et al. (2003).

Because the raw gas feeding the AGE absorber is itself high in CO_2 , and the CO_2 content progressively increases as the gas traverses the tower, the partial pressure contribution to the driving force for CO_2 absorption is always high. Conversely, H_2S concentration is already low in the raw gas (which is why enrichment is being done) and it gets lower still as the gas passes through the contactor, reaching (we hope) ppm levels at the top. Thus the partial pressure driving force for H_2S absorption is relatively low. The other part of the driving force for absorption is the partial pressures exerted by partially loaded solvents. As succinctly put by Johnson et al. (1992), in part quoting Astarita et al. (1983, 1986), "The equilibrium solubility of H_2S in chemical solvents such as MDEA is not much higher than the solubility of CO_2 . Since chemical solvents do not have significant thermodynamic selectivity, they must rely on the difference in rates of absorption of H_2S and CO_2 to obtain the desired process selectivity (emphasis added)."

The differences in absorption rates are determined partly by phase equilibrium, partly by reaction kinetics, and partly by the hydraulic and mass transfer characteristics of the contacting equipment vis à vis the relative magnitudes of gas- and liquid-side mass transfer coefficients. None of these factors operates in isolation from the others – they are all equally important

to determining the actual mass transfer rates occurring at each point in the contactor.

Kinetically, H_2S absorption is accompanied by an instantaneous proton transfer reaction associated with H_2S dissociation and amine protonation. On the other hand, CO_2 reacts at finite rates, and in the case of selective amines very slowly indeed, forming bicarbonate ion but no amine carbamate. Their relative reaction rates are at opposite ends of the spectrum.

As far as equipment is concerned, trays and packing (both random and structured) exhibit quite different hydraulics and, therefore, should be expected to have different mass transfer characteristics with respect to relative gas- and liquid-phase resistances. Because the main mass-transfer resistance to H_2S absorption is in the gas phase while for CO_2 it is in the liquid phase, relative absorption rates are affected by the type and mechanical details of the contacting equipment itself. Suffice it to note that AGE is a process controlled by mass transfer rates, and only a true heat- and mass-transfer-rate based model stands any realistic chance of actually predicting performance.

The only amine-based solvents that make any sense in this application are ones that do not react with CO_2 to form carbamates. This means tertiary and sterically hindered amines are the only contenders and, of these, MDEA (perhaps assisted by partial neutralisation) and the hindered amines are the only realistic candidates in AGE applications. Because the hindered amines currently in commercial use are all members of the FLEXSORB family and are proprietary to ExxonMobil Corporation, this paper focuses on

generic MDEA, including phosphoric acid as a promoter¹.

Regenerated acid gas is usually available within a fairly narrow pressure and temperature range: between 5 and 20 psig and 100°F to 120°F. Components are limited to H₂S, CO₂ and water with only trace amounts of other components such as heavy hydrocarbons, BTEX and inerts. The H₂S content ranges from a few mol% for only slightly sour wellhead gases (hundreds of ppmv) to many tens of mol% when the well produces gas with a high H₂S:CO₂ ratio. The rest of the feed to the AGE unit is CO₂ with enough water to saturate the gas at the temperature and pressure of the overhead condenser on the gas reacting stripper. Trace amounts of contaminants have no effect on AGE unit performance, save for those that exhibit surface activity, and which are excluded from the scope of this discussion.

The two examples to follow illustrate typical AGE operations and quantify the ability of simulation using a mass and heat transfer rate model to predict performance. These examples naturally suggest process improvements and they raise many questions concerning what more optimal conditions might be, whether another choice of contactor internals could have yielded better results, and whether generic MDEA

could have been improved upon, to name a few.

Some process configurations

In terms of process configuration, the AGE absorber is typically in the same amine circuit as the TGCU or SCOT unit because they make similar demands on solvent purity, both require a maximally selective solvent, and both are relatively low-pressure operations. The amine circuit for these units is usually separate from the main gas treating plant simply because the SCOT and AGE contactors make different demands on the amine than the primary high-pressure treating plant does. In fact, the main treating plant may use a different amine altogether.

Standalone AGE

The first and most obvious processing scheme is a standalone AGE unit, perhaps utilising a lean amine stream from the same regenerator as the TGCU. Figure 1 shows the simplest example. The gas being upgraded contains only 20% H₂S, far from ideal for an SRU. The other conditions shown in the figure are a snapshot of operations on a particular day. There were insufficient data even to check an overall material balance, let alone component balances. The flowsheet was simulated using the proprietary ProTreat from Optimized

Gas Treating, Inc., with the reboiler duty adjusted to reproduce the regenerator's reported reflux flow. As is typical, useful operating data are extremely hard to come by for AGE units, probably because no one wants to handle gas samples having high H₂S levels. In this particular case, no solvent sample analyses were available, nor was the H₂S content of the SRU feed gas measured, so the only measurement available was the treated gas H₂S concentration, reported to be less than 100 ppmv. ProTreat simulation predicted a value of 43 ppmv in agreement with reported plant performance. Plant CO₂ slip was unknown. However, ProTreat predicted 85% slip, which seems to be fairly typical for low-pressure selective treating. The regenerator molar-reflux ratio was calculated to be very close to unity, which, for achieving low residual H₂S loading, is not particularly vigorous regeneration. Simulated residual loadings were 0.0008 and 0.001 for H₂S and CO₂ respectively. For a solvent using phosphoric acid as a stripping promoter, these are not especially low numbers. However, without the phosphoric acid promoter, predicted lean loadings are 0.008 and 0.04 mol/mol, respectively, roughly a factor of between 10 and 40 times higher than with enhanced stripping. Furthermore,

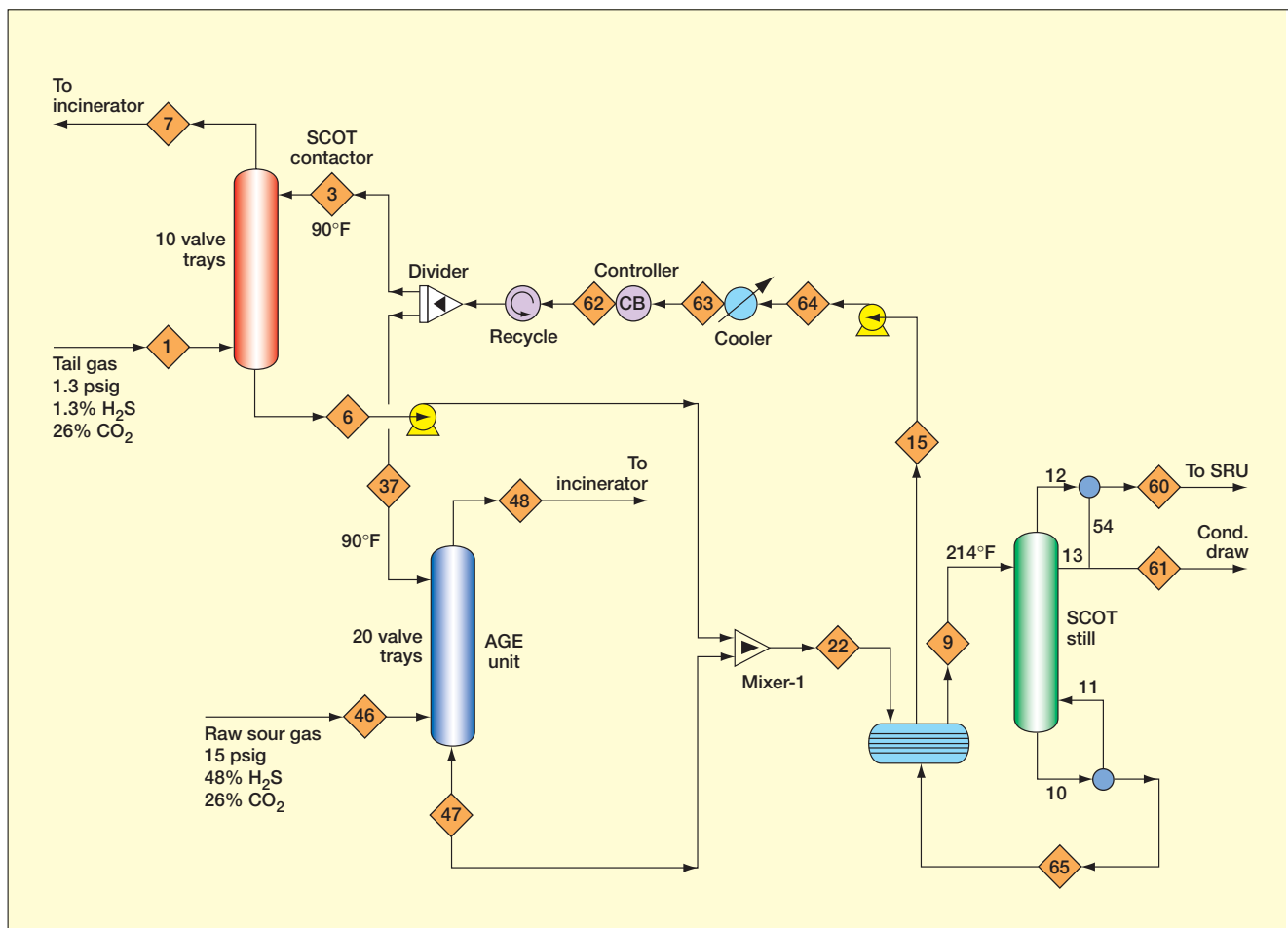


Figure 2 AGE and SCOT units with common regenerator

Effect of changes to process variables on unit and plant performance (constant total circulation rate)

	1 Base (50% MDEA)	2 Base + H ₃ PO ₄	3 Base with 2x Amine to SCOT	4 Case 2 with 2x Amine to SCOT	5 Case 4 at 10% more reboiler duty
SCOT Leak H ₂ S (ppmv)	445	1,044	283	104	45
AGE Leak H ₂ S (ppmv)	101	6	294	98	40
Lean Load H ₂ S (m/m)	0.0047	0.00014	0.01	0.0012	0.0005
Lean Load CO ₂ (m/m)	0.00013	0.000098	0.0002	0.00005	0.000038
SRU Feed (% H ₂ S Dry)	82.9	75.7	82.0	82.7	82.7
Sulphur Emission (lb/hr)	4.41	9.96	3.21	1.16	0.51

Table 1

the treated gas H₂S leak would have been nearly 200 ppmv.

SCOT and AGE units with common regenerator

The design and ultimate performance of an AGE unit depends on lean amine quality, something that can only be established if the SCOT unit is included as well. Figure 2 shows a PFD of SCOT and AGE units combined in the simplest way possible – just connected through, and served by, a common regenerator. The data shown in the figure are for an existing plant. The sour gas to the AGE unit is already fairly rich in H₂S. Nevertheless, it is being further enriched because of the benefits to sulphur recovery. This plant is operating with 50 wt% generic MDEA. Again, data are scanty except to say that the SCOT unit is leaking several hundred ppmv and the AGE is treating down to around 100 ppmv. Both these figures were confirmed by ProTreat simulation, which predicted 445 ppmv and 101 ppmv H₂S leak from the SCOT and AGE units respectively. No information was available on the gas stream to the SRU, although ProTreat predicted nearly 83% H₂S on a dry basis, with 96% and 83% CO₂ slip through the SCOT and AGE units respectively. Simulation results for this and other scenarios are shown in Table 1.

The tail gas treater is the bigger contributor to sulphur emissions because of its high total flow rate and higher residual H₂S content. Simulation showed the SCOT contactor to have close to the optimal number of trays; with too few trays providing too little contact to remove the maximum amount of H₂S, and too many trays allowing too much CO₂ absorption, and using up too much solvent loading capacity. The important finding from simulation, however, was that the SCOT contactor was not lean-end pinched. In other words, the solvent lean loading was not setting the H₂S leak. Rather, the mass transfer rates themselves were.

The importance of the difference

between lean-end pinching and mass transfer rate limitations became abundantly evident when a few thousand ppmw of H₃PO₄ was added as a stripping promoter to the solvent in the simulation. Under otherwise identical conditions, and despite the additive reducing the lean solvent H₂S loading from 0.0047 to 0.00014 mol/mol, the H₂S leak from the SCOT absorber actually deteriorated from 445 ppmv to over 1,000 ppmv. The reason: the reduced lean loading is more than compensated by the increased H₂S back-pressure at absorber temperatures, so H₂S mass transfer (absorption) rates throughout the column fall. This is perhaps indicative of rich-end pinching. Turning to the AGE unit, however, the H₂S leak from the AGE column was improved from 100 ppmv to 6 ppmv because the mass transfer rates are overshadowed by the fact that the AGE is completely lean-end pinched with respect to H₂S. In other words, the effect of reduced lean solvent loading of H₂S has full impact at the lean end of the AGE absorber. The important lesson to be learned from this exercise is that for a stripping additive to be fully effective, all the columns served by the common solvent must be designed and operated for lean-end pinch conditions.

The problem with using an additive to reduce H₂S leak in this case is that the additive causes a deterioration in SCOT column performance that exceeds its benefit to the AGE column. If the additive is to be made effective, the SCOT column therefore must be forced into a lean-end-pinched state. Undoubtedly, this can be done in several ways – the one chosen here for illustration was to double (arbitrarily) the solvent flow to the SCOT absorber. This may seem radical. However, the AGE handles more than 15 times the H₂S fed to the SCOT unit, so doubling the smaller of two flows does not add tremendously to the total circulation rate through the plant. Column 3 of

Table 1 shows just how little a doubling of the solvent flow to the SCOT column affects performance without additive, with all other conditions including reboiler energy fixed. However, the higher flow increases stripping effectiveness of the additive itself (Column 4). Solvent stripping is still not what it could be – Column 5 of Table 1 shows the effect of a 10% increase in reboiler duty; a further 10% lowers both H₂S leaks by half again.

None of these cases is meant to represent optimal conditions – they are illustrative and are intended only to indicate directionality, and the sort of performance changes that result from corresponding changes in process parameters. Granted that the results in Table 1 are simulations. However, the extent to which the ProTreat simulations agree with the rather limited plant performance data lends comfort that they are probably fairly accurate across the board.

Part II

In Part II of this article, comparisons will be made with new commercial plant operating data as well as with information presented at a Laurence Reid Gas Conditioning Conference. Apart from a final example in Part II, exploring other processing schemes occupies most of the remainder of the discussion. Comparisons will be made with new commercial plant operating data as well as with information presented at another Laurence Reid Gas Conditioning Conference. In addition, a rather clever recycle scheme is examined from the perspective of likely recycle ratios and regeneration energies needed for various improvements.

Note

1. There is a wealth of data on the hindered amine 2-amino-2-methyl-1-propanol (AMP) but this chemical does not appear to have found commercial use.