



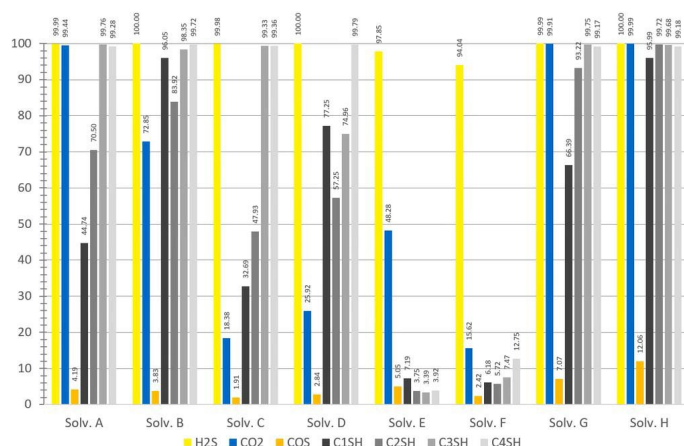
Removing Sulfur Compounds from Gases



Sulfolane is a cyclic sulfone with the formula $(CH_2)_4SO_2$ and the chemical structure shown here. It has *high affinity for certain sulphur-containing compounds and aromatics*, but low affinity for aliphatics. Indeed, it has been used for many years as an extractive agent for the selective removal of aromatics from liquid hydrocarbons. To date, sulfolane appears to be the only physical solvent added to aqueous amine mixtures to improve the absorption and removal of certain components. Commercially, mixed solvents using sulfolane bear the trade-name Sulfinol (-D, -M, -X, as developed by the Shell Oil Company. More generically, solvents consisting of water, an amine and *any* physical solvent are called Hybrid Solvents.



The Sulfinol class of solvents shows greater affinity for the acid gases than their aqueous amine equivalents (mostly H_2S but to varying extents, CO_2 as well). The bar charts in Figures 1 and 2 compare several Hybrid Solvent formulations used in a trayed and a packed tower, respectively. The plots are qualitatively similar but quantitatively the effect of sulfolane is somewhat less with packing. The crucial observation, though, is that using sulfolane at commercial strengths appears always to improve mercaptans absorption (usually markedly, but depending on the amine) and has a very much more marginal effect on COS removal. The question is why. The mercaptans, COS, and sulfolane are all sulfur-containing so there is implied compatibility. What causes COS to behave so differently?



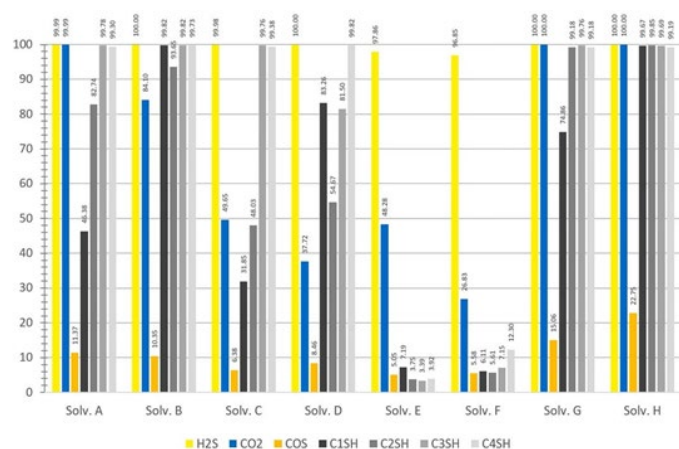
- Solvent A 45 wt% MDEA, 5 wt% PZ, 35 wt% Sulfolane
- Solvent B 45 wt% DIPA, 5 wt% PZ, 35 wt% Sulfolane
- Solvent C 45 wt% MDEA, 35 wt% Sulfolane
- Solvent D 45 wt% DIPA, 35 wt% Sulfolane
- Solvent E 50 wt% DIPA, (chemical solvent)
- Solvent F 50 wt% MDEA (chemical solvent)
- Solvent G 45 wt% MDEA, 8 wt% PZ, 35 wt% Sulfolane
- Solvent H 40 wt% MDEA, 10 wt% PZ, 40 wt% Sulfolane

Figure 2 Percentage of RSH and COS Removed by Various Hybrid Solvent Formulations (Packed Tower)

Mercaptans have a weak S–H bond and solubilize in water with the instantaneous liberation of a hydrogen ion, i.e., they deprotonate. Although mercaptans are only sparingly soluble in water, their absorption rate is controlled entirely by the gas-side mass transfer resistance because mercaptans per se barely exist in the water phase at all — they offer no liquid-side resistance because they immediately vanish by being converted to mercaptide (which is not the species being absorbed). Absorption rate is *not* controlled by reaction rate. Carbonyl sulfide is completely different.

In carbonyl sulfide, oxygen and sulfur are connected to a central carbon atom via covalent double bonds, forming a linear molecule ($O=C=S$). COS dissolves into water via Henry's Law. Its absorption rate is not enhanced by reaction because, although in an overall sense COS decomposes into CO_2 and H_2S by reacting with water, it does so *extremely slowly* — too slowly to have any effect on its absorption rate via enhancement through chemical reaction. In the time frame of contacting in mass transfer devices containing trays or packing, COS absorbs physically to its Henry's Law saturation point, and no further. However, when the solvent is alkaline, that all changes.

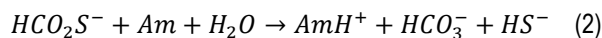
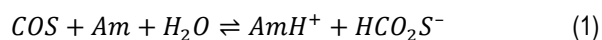
Under alkaline conditions, the proton liberated by mercaptan is neutralized by the alkaline component, be it OH^- , $-N$, $-NH$, or $-NH_2$, thus allowing the mercaptan to continue being absorbed for as long as there is sufficient alkalinity left for the proton sink (the amine) to remain active. There is an altogether different mechanism for COS removal.



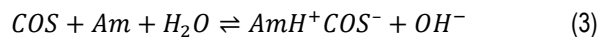
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Figure 1 Percentage of RSH and COS Removed by Various Hybrid Solvent Formulations (Trayed Tower)

In the presence of amines, it's postulated that COS reacts by a base-catalysed mechanism†:



In addition to these reactions, COS forms thiocarbamate ($AmCOS^-$) with primary and secondary amines via a zwitterion mechanism — thiocarbamate formation is the critically important step in COS absorption:



Equation (3) represents the zwitterion mechanism and Equation (4) describes its deprotonation. Any base, B, present in solution deprotonates the zwitterion.

The rate of thiocarbamate formation is significantly limited by the deprotonation reaction (4). In fact, for several amines, the COS absorption rate is almost completely determined by the rate of deprotonation. This is unlike CO_2 where the zwitterion deprotonation rate has a much lesser influence. As a result of these factors, it's reported that the COS-amine reaction rate is roughly two orders of magnitude slower than CO_2 . Nevertheless, COS reaction rates are significant enough for a substantial fraction of the COS in a typical feed gas to be removed by primary and secondary (but not tertiary) amines. *Deprotonation kinetics are amine dependent.* In addition, of course, the physical solubility of COS in a given solvent depends on its composition as well as the components it contains.

The belief seems to be a fairly widely held that COS and mercaptans, all being sulfur compounds, should have similar removal rates in amine systems, and that the rates ought to be fairly independent of the particular amine. The physical chemistry presented here should go some way to dispelling these myths. These are ill-founded and invalid expectations that should be replaced by the following:

- COS and mercaptans are all sulfur compounds but they have inherently different structures and so they don't behave the same way in aqueous amine solutions;
- Removal rates of COS and mercaptans should be expected to be quite different;
- Various amines have different thiocarbamate reaction kinetic rates so COS removal rates should depend on the amine;
- RSH absorption relies on dissociation into H^+ and RS^- ions. COS absorption relies on thiocarbamate formation. Different chemistry means different absorption rates and different extents of removal;
- Chemically, COS absorption by amines is a lot more complex than meets the eye so extrapolation to similarities with mercaptans is really a gross oversimplification.

Effective Amines for COS Removal

Amines that are best for CO_2 removal tend to be best for removing COS, too, and those that are best suited to promoting CO_2 slip have the poorest ability to absorb COS. Primary and secondary amines are carbamate and thiocarbamate formers with CO_2 and COS, with CO_2 reaction kinetics about two orders of magnitude faster. The result is that the fastest carbamate formers are also preferred for COS absorption. This can present a quandary. If the application demands selectivity for H_2S (and therefore CO_2 rejection), the solvent of choice will be a non-carbamate former such as MDEA. But this is probably the worst possible choice for

removing COS and, in most circumstances, probably precludes highly selective H_2S removal when COS removal is also wanted.

An absorption system intended to remove CO_2 to low levels may be unable to treat the same gas to low residual COS content. Frequently a small concentration of piperazine is added to an MDEA solvent to promote reactivity and allow MDEA (with its low regeneration energy requirement) to be used for deep CO_2 removal. Piperazine is many times more reactive with CO_2 than even MEA so is quite effective as an MDEA activator. However, because it is at low strength when used as a promoter, the piperazine component quickly becomes used up and, although it remains effective for CO_2 removal, slower reaction kinetics means its efficacy falls off when it comes to removing COS. Solvents A, G and H in Figures 1 and 2 show that for 5, 8 and 10 wt% piperazine, percentage COS removal increases with piperazine strength (11, 15, 22% for trays, and 4, 7, 12% for packing) roughly in proportion to the piperazine content. As shown previously (*The Contactor*, Vol. 16, No. 5), the actual amine being used makes a huge difference to a given absorber's ability to remove COS.

Packing or Trays

In terms of slipping CO_2 , packing tends to be a somewhat better choice for absorber internals than trays. This has to do with the mass transfer characteristics of a smooth film flow (packing) vs. a very agitated liquid (trays). Packing generates numerically smaller liquid-film coefficients for the film flow.

As Figures 1 and 2 show for solvents A, G and H, trays are twice as effective as packing for COS removal in this particular case. The learning here is that although COS removal is greatly influenced by the *kinetics* of thiocarbamate reaction, inherent resistance to mass transfer in any system with a significant diffusional challenge must equally be taken into account. This makes COS absorption very much a process involving mass transfer with chemical reaction. Whether it's the gas-side or liquid-side mass transfer resistance that matters the most depends on the transferring component. Instantaneous reaction in the liquid makes the gas phase controlling for mercaptans absorption while slow reaction makes the liquid phase controlling for COS absorption.

The OGT | ProTreat® mass transfer rate-based model for mercaptans and COS absorption allows you to accurately predict just how solvent choice, composition, and choice of column internals will affect the ability to remove COS and mercaptans to satisfactory levels.

To learn more about this and other aspects of gas treating, plan to attend one of our on-line training seminars or in-person workshops. For details visit www.oqtr.com/training.

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† These reactions can be written with equal validity using OH^- instead of Amine.