Upgrading acid gas streams

Using the ProTreat™ amine simulator, **T. K. Khanmamedov** of TKK Company and **R. H. Weiland** of Optimized Gas Treating, Inc. analyse how Highsulf™ can produce a Claus plant feedstock of excellent quality from sour gas streams such as sulphur plant tail gas and raw gases that would otherwise present disposal problems.

In many instances it is not possible to remove the hydrogen sulphide from a gas stream and simultaneously produce a satisfactory sulphur plant feed using conventional gas treating technology. In these cases the H_2S, once removed from the gas, can present a serious disposal problem because its concentration in the product acid gas stream is too low to be fed to a sulphur plant but is far too high to be incinerated. One option is to treat selectively the acid gas stream itself and raise its H_2S content to a level suitable for a sulphur recovery unit. However, conventional enriching of the acid gas stream may still fail to yield satisfactory results.

Sulphur plants operate best with a feed containing 55% or more H_2S. The balance of the SRU feed stream is CO_2 and water, with small amounts of hydrocarbons, inerts, and other components. Lower concentrations of H_2S can be processed only with increasing levels of sulphur plant complexity, larger equipment, and higher cost. Streams having less than 32% or so H_2S are near the lower limit for a straight-through Claus process.

There are numerous sources of acid gas streams that are too dilute for sulphur recovery in Claus plants but too concentrated to vent. In plants treating high CO_2:H_2S ratio gas, adequate CO_2 slip even using the most selective solvent often cannot produce an SRU feed of sufficient quality. For example, conventional treatment of a high pressure gas containing 1-2% CO_2 and a few 100s of ppmv H_2S using even the most selective amine available cannot produce an acid gas stream with more than a few mol-% H_2S, completely inadequate for a conventional Claus SRU. Even in plants with a moderate CO_2:H_2S ratio of say 4:1, if complete acid gas removal is necessary (LNG for example), using a single contactor will necessarily produce an acid gas stream containing only 20% H_2S.

Highsulf™ (a trademark of the TKK Company) is a patented process strategy that can be applied incrementally in amine treating plants to increase the H_2S concentration in the off-gas from the regenerator and produce an increasingly high quality Claus sulphur plant feed.[1-6] Some computer simulation runs of the Highsulf process, using the ProTreat™ (trademark of Optimized Gas Treating, Inc.) simulator, were presented, discussed, analysed and published by Weiland[14,15]. A conventional amine treating plant (in this instance, a tail gas treater, or TGTU) is shown in simplified form in Fig. 1. The tail gas is sulphur plant effluent, essentially a stream of H_2S and CO_2 diluted with the nitrogen remaining after the combustion and catalytic processes that convert H_2S into elemental sulphur in a Claus sulphur plant. Frequently, the off-gas is of only very marginal quality as a sulphur plant feed. There are two approaches to making it more suitable. One is to apply various levels of Highsulf directly to the TGTU. The other is to reprocess the off-gas in another, smaller amine plant and produce by selective absorption a second off-gas of higher quality. This secondary treating unit (also called an acid gas enrichment, or AGE, unit) may also apply the Highsulf strategy. Highsulf recognises that the higher the H_2S content of the gas being treated in an amine unit, the greater will be the H_2S concentration in the off-gas from the regenerator. Highsulf processes produce a more concentrated product stream, as discussed by Khanmamedov[7-9].

The role of selectivity

Achieving the maximum selectivity for H_2S over CO_2 is done by using the right solvent under the right process conditions in the right equipment. It is paramount to successful tail gas treatment and to the operation of AGE units. The perfect process in these applications removes all the H_2S and none of the CO_2 from the raw gas because an acid gas consisting entirely of wet H_2S is produced upon solvent regeneration. This would be perfect selectivity. Detailed discussions of selectivity have been presented in many places including Khanmamedov[7, 9], Anderson et al.[10] and Weiland et al.[11], so only a brief review is given here.

The equilibrium solubilities of H_2S and CO_2 in selective solvents such as methyldiethanolamine (MDEA) do not differ radically. In other words, chemical solvents do not have great thermodynamic selectivity so vapour-liquid equilibrium does not play as critical a role as one might suppose. The differences in absorption rates are really determined 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. The mass transfer characteristics of the contacting equipment have been largely overlooked by many practitioners, possibly because of poor understanding of separation equipment from the standpoint of its inherent mass transfer rates and what affects them.

Tertiary amines, of which MDEA is the most commonly used in selective treating, react with H_2S and CO_2 at chemical rates that are at opposite ends of the spectrum. H_2S absorption is accompanied by an instantaneous proton transfer reaction associated with H_2S dissociation and amine protonation. Carbon dioxide, on the other hand, reacts very slowly indeed, forming bicarbonate ion by reaction with water, but no amine carbamate. Thus, from a reaction kinetic standpoint, MDEA is highly selective for H_2S.

As devices for carrying out mass transfer, trays and packing (both random and structured) behave quite differently hydraulically. The most obvious reason for this difference is that a properly operating tray (froth regime, not spray regime) usually has the liquid phase continuous and the gas phase dispersed, while in packing the opposite is generally true. The liquid flows over packing in films that are relatively quiescent compared to the highly agitated state of the liquid flowing across trays. Vapour flows are quite turbulent for both trays and packing. Therefore, these types of equipment should be expected to have different mass transfer characteristics, most pronounced with respect to their relative liquid-phase resistances, but also with respect to their vapour-phase resistances (to an extent that depends greatly on the exact internals involved). These differences in characteristics are important to establishing selectivity because the mass-transfer resistance to H_2S absorption is primarily in the gas phase, while for CO_2 it is in the liquid phase. The result is that to some extent selectivity can be controlled by controlling the relative resistances to mass transfer offered by the two phases through the judicious selection of tower internals. Phase resistances are functions of the type (trays, random packing, structured packing) and mechanical details (tray passes, weir heights, packing brand, size, crimp angle, etc.) of the contacting equipment itself as well as the way it is operated hydraulically (flow rates and phase properties that depend on temperature and pressure). Tail gas treating and acid gas enrichment are processes whose performance is completely dependent on relative rates of mass transfer. Only a true heat- and mass-transfer-rate based model such as ProTreat™ stands any realistic chance of reliably predicting performance in a specific piece of equipment. Reliable simulations cannot be done unless the simulation tool itself is cognisant of the mass transfer behaviour of the internals, and the engineer doing the calculations also keeps in mind the hydraulic regime in which the column is operating (e.g., spray versus froth regimes for trays).

All amines instantly react with (i.e., are protonated by) H_2S, so selectivity is a function of the reaction rate of CO_2 with the amine. Because CO_2 does not react with tertiary and sterically-hindered amines, these are the only amine-based solvents that make any sense in highly selective treating applications such as TGTUs and AGEs. Commercially, this makes them the only contenders, with MDEA (perhaps assisted by partial neutralisation) and the hindered amines being the only realistic candidates. Because the hindered amines currently in commercial use are all members of the Flexsorb® family and are proprietary to ExxonMobil Corporation, the remainder of this article focuses on generic MDEA, including phosphoric acid as a promoter.

Two applications of Highsulf are considered, tail gas treating and acid gas enrichment. In both applications, in addition to examining the effect of Highsulf on SRU feed quality, scrutiny is also given to the value of phosphoric acid as a stripping promoter.

Tail gas treating

The base-case unit is a conventional TGTU using 35 wt-% MDEA. The 6-ft diameter contactor is packed with 20-ft of Flexipac® 2Y structured packing. The regenerator is 6-ft diameter and it contains 30 generic one-pass valve trays. A process flow diagram is shown in Fig. 1.

The tail gas is 1% H_2S and 3.4% CO_2, balance nitrogen and trace inerts, and is flowing at 3 MMSCFD and a pressure of 1 psig. The solvent flow to the regenerator is 94 US gpm and it is preheated in the cross-exchanger to 205°F. These basic parameters correspond to an actual TGTU in a refinery. Under these conditions, the treated gas going to incineration was about 50 ppmv H_2S, which corresponds fairly closely to the simulation value of 52.6 ppmv. Although its composition was not measured, the feed to the SRU is simulated to be 37.8 mol-% H_2S, 54.9% CO_2, the balance being water vapour and a trace of nitrogen, and essentially the same numbers result from a component balance around the entire TGTU. Although this gas is certainly suitable as an SRU feed, the SRU could be hydraulically unloaded and its performance streamlined if the feed were richer in H_2S. Highsulf is a way to achieve this.

Table 1 shows a comparison between this base case (Case 0) and the more important performance metrics that result when Highsulf is applied to increasing extents. The percent CO_2 slipped through the absorber is based on the tail gas feeding the column and the CO_2 flow in the gas to incineration.

Vigorously applying Highsulf (Cases 5 and 6) almost doubles the H_2S content of the SRU feed, from 38% to about 70% and still maintains the gas to incineration at below 100 ppmv. But the system collapses for Case 6. It is important to point out that as Highsulf is applied with increasing vigour, nothing else in the simulated plant was changed—the important parameters of

Fig 1: **Tail gas treating unit**

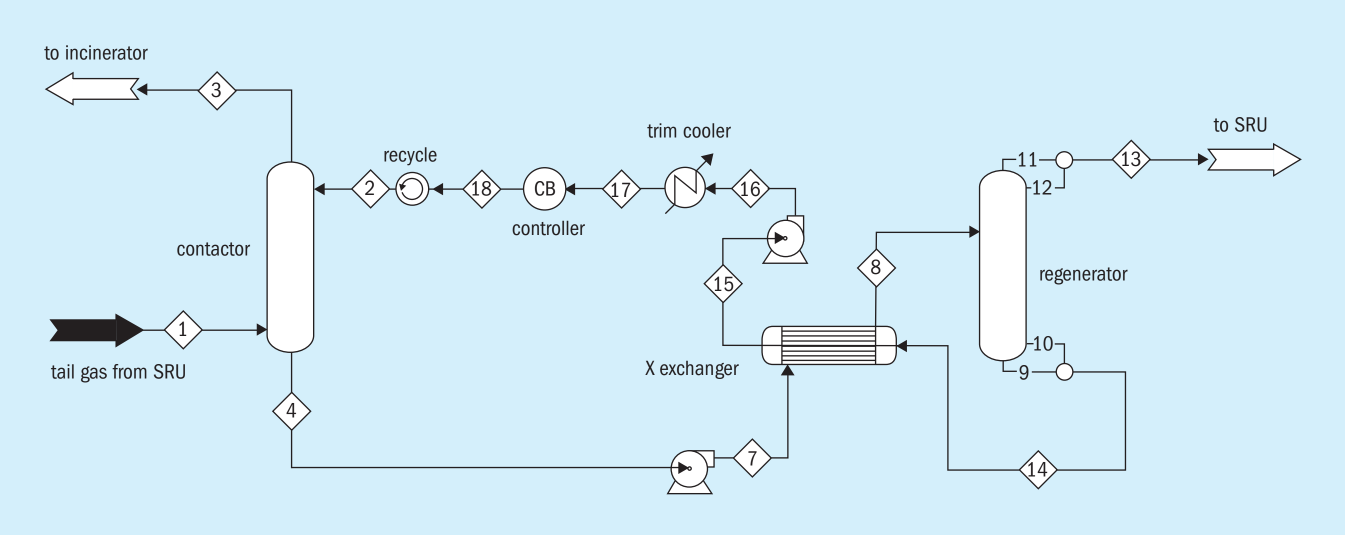


Table 1: **Effect of Using Highsulf technology on TGTU Performance**

Case	**Relative extent of Highsulf application**						
	0	1	2	3	4	5	6
H_2S in SRU Feed (%)	37.9	41.1	45.6	52.7	65.4	70.4	75.9
H_2S to Incineration (ppmv)	53.2	55.5	58.5	65.1	85.3	130	1,600
CO_2 Slipped (%)	57.7	63.3	69.9	78.0	88.0	91.0	94.9

Table 2: **Effect of using Highsulf technology on TGTU performance when a stripping promoter is used**

Case	**Relative extent of Highsulf application**						
	0	1	2	3	4	5	6
H_2S in SRU Feed (%)	38.6	41.8	46.4	53.6	66.3	71.4	77.7
H_2S to Incineration (ppmv)	5.3	6.4	7.3	9.3	16.6	40.2	1,520
CO_2 Slipped (%)	58.8	64.2	70.8	78.7	88.5	91.4	95.4

Fig 2: **Profiles of H_2S concentration in the TGTU contactor for various extents of Highsulf application**

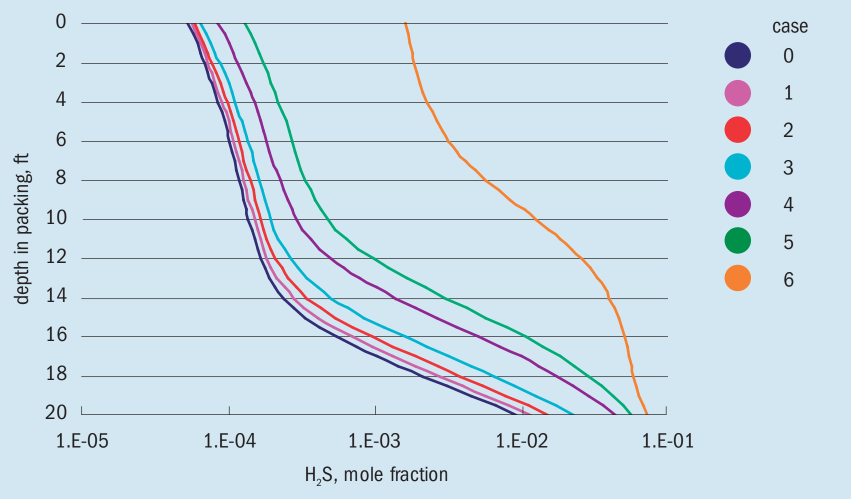
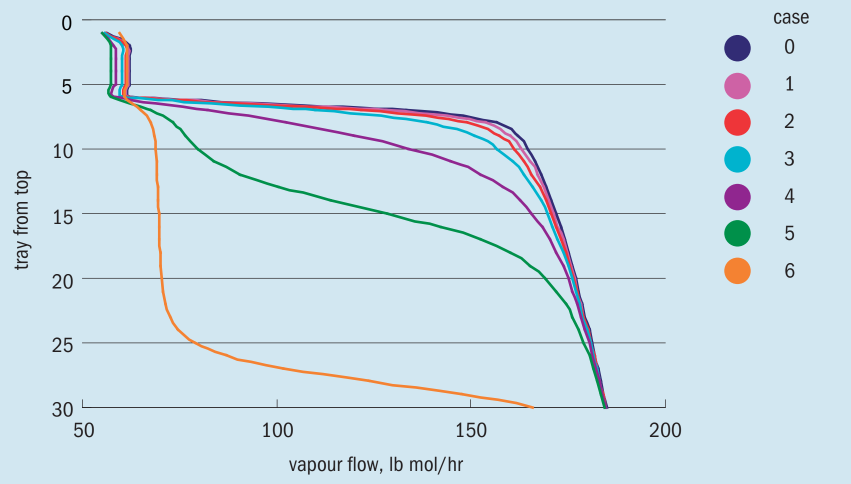


Fig 3: **Vapour flow through regenerator as a function of Highsulf application**



reboiler duty and solvent circulation rate, as well as all other parameters, were held fixed so there is no operating cost associated with this application of Highsulf. It's not a great oversimplification to say that nothing much more than a minor rerouting of piping is needed to achieve a truly remarkable increase in SRU feed quality.

It is instructive to enquire as to the cause of the escalation in the H_2S level in the treated gas. Figure 2 shows profiles of H_2S in the gas versus position down the packed bed corresponding to the various cases in Table 1. For Cases 0 through 5, the H_2S profiles shift to higher concentrations more or less in proportion to how vigorously Highsulf is applied. However, when Highsulf is over-applied, the column goes from lean-end to rich-end pinched and H_2S breaks through into the incinerator gas. The breakthrough is precipitous. The relative flatness of the profiles at the lean end (top) of the column is witness to the lean-end pinch condition. The flatness at the rich end in Case 6 indicates a rich-end pinch condition.

Figure 3 shows that in Case 5 the vapour flow through the regenerator begins to collapse. By Case 6, the reboiler with its constant duty is unable to keep up with the demand for stripping steam and all the vapour generated is consumed over the bottom five trays, with none being left to do any further stripping over the 20 stripping trays above. The top five trays in this column are wash trays, rich amine entering onto the sixth tray from the top.

With all other conditions constant, there is a limit to how vigorously Highsulf can be applied before the operation collapses. However, it is remarkable that when the optimal extent of Highsulf is applied, the SRU feed quality can be nearly doubled for zero operating cost.

The fact that the TGTU contactor is lean-end pinched says that the H_2S leak to incineration is determined by lean-amine acid-gas loadings and this suggests that using a stripping promoter will help achieve a reduced H_2S. The most commonly used stripping promoter is phosphoric acid, proposed in a patent to Dibble[12]. Typically, concentrations below about 1 wt-% are used. The mechanism by which small quantities of organic and inorganic acids (including heat stable salts) achieve great reductions in residual acid gas loadings in stripped solvents has been described in detail by Hatcher et al.[13] and Weiland[14,15]. Briefly, small amounts of acid permanently protonate a small fraction of the amine. At

Table 3: **Effect of Highsulf processing on AGE performance**

Case	Relative extent of Highsulf application						
	0	1	2	3	4	5	6
H_2S in SRU Feed (%)	28.6	32.9	38.9	48.3	66.1	76.3	78.3
Mass flow to SRU (lb/hr)	1,488	1,283	1,068	840	586	464	313
H_2S to Incineration (ppmv)	19.1	24.9	34.6	52.5	90.2	4,490	27,400
CO_2 Slipped (%)	80.0	83.6	87.5	91.6	96.2	98.0	98.8

Table 4: **Effect of H_3PO_4 on Highsulf performance in AGE**

Case	Relative extent of Highsulf application						
	0	1	2	3	4	5	6
H_2S in SRU Feed (%)	29.1	33.4	39.5	48.9	67.2	73.0	76.0
Mass flow to SRU (lb/hr)	1,463	1,262	1,051	829	575	519	447
H_2S to Incineration (ppmv)	0.5	0.6	0.7	1.0	4.1	380	8,160
CO_2 Slipped (%)	80.4	84.0	87.8	91.9	96.4	97.4	98.1

the very low loadings typical of the reboiler in a regenerator, the amount of protonated amine is extremely small. Artificially increasing it by using an acid drives the decomposition reaction to the left, towards free unreacted acid gas, removing still more H_2S from the solution.

The work already described was repeated with 3,000 ppmw phosphoric acid added to the same 35 wt-% MDEA solvent. Nothing else was altered in any way. The performance measures shown in Table 1 are repeated in Table 2 after the stripping promoter is added.

Comparison with Table 1 shows a trivially small effect of the phosphoric acid additive on SRU feed quality; however, H_2S leak to incineration is reduced by factors of between 3 and 5 until once again the process collapses under the load of excessively applied Highsulf, when the contactor goes into a rich-end pinched state and H_2S breaks through. The reason H_2S leak rates to incineration are so greatly reduced is that the lean solvent loading of H_2S, is lowered by factors of between 15 (Case 5) and more than 30 (Case 0 with no Highsulf application). These reductions do not translate fully into lowered H_2S leak values because the phosphate additive also increases the H_2S backpressure in the absorber. However, the effect of reduced lean loading exceeds that of elevated H_2S backpressure, and the result is still a very substantial reduction in H_2S leak from the contactor. Incidentally, the same effect has been observed in plants with similar levels of heat stable salts, and occasionally a plant will fail to meet treating specifications immediately after an aggressive solvent reclaiming operation because the stripping promoters have been removed.

Highsulf also results in a substantial reduction in the total gas flow to the SRU while maintaining essentially the same flow of H_2S. For example, in Case 4, the SRU processes only one-half the total gas that there would be without Highsulf. In the present case, Highsulf enables nearly a doubling in SRU feed quality and at the same time it unloads the sulphur plant by 50%. Its operating cost is zero, and negligible capital investment. Rarely is nature so gratuitous.

Acid gas enrichment

The acid gas enrichment (AGE) plant is schematically identical with the TGTU shown in Figure 1 except that now the feed to the contactor is actually a relatively dilute stream of H_2S in wet CO_2 coming from the regenerator of a conventional gas treating plant. In this example, the contactor contains 20 valve trays in a 4-ft diameter shell and operates at 3 psig. The regenerator is at 20 psig and it has 23 stripping trays (valve trays at 24-in tray space) and 5 wash trays (bubble-cap trays at 30-in tray space) in a 4.5-ft diameter shell. In the base case (Case 0) where Highsulf is not used at all, both columns operate at about 25% of jet and downcomer-choke flood so they are operating in the froth regime. Raw gas enters the contactor at 495 ft^3/min, 120°F and 15 psig, with 8 mol-% H_2S and 92 mol-% CO_2 on a dry basis and is water saturated. The solvent is 50 wt-% MDEA at 100 US gpm and 90°F. The reboiler uses 6,000 lb/h of 65 psig steam. These data correspond to an actual operating plant. As Highsulf is applied with increasing vigour (Cases 2 – 6), the basic operating parameters are kept constant so the effect of increasing the extent of Highsulf application alone can be isolated.

Table 3 shows performance metrics for the base case, how various degrees of Highsulf application improve enrichment, and the cost in terms of increased H_2S leak to incineration. Just as for the tail gas treating example, CO_2 slip through the absorber is assessed on the basis of the raw gas feeding the column and the gas to incineration.

As Highsulf continues to be applied more vigorously, the quality of the SRU feed steadily climbs and by Case 4 it contains nearly two and a half times the concentration of H_2S. As shown in Fig. 4, at levels of application beyond Case 4, the H_2S leak goes through the roof so Case 4 represents the practical maximum enrichment unless other process conditions are changed.

Figure 5 shows how Highsulf can enhance SRU feed quality. At the same time, the total gas load on the SRU decreases by 60%. And all of this is achieved by Highsulf at zero operating cost and next-to-zero capital investment.

In addition, the Highsulf system provides a simple and very stable means of controlling the degree of enrichment and the amount of H_2S leakage from the AGE unit's contactor[2, 3].

The contactor in this AGE unit is also lean-end pinched so phosphoric acid can also be used here to improve solvent regeneration and thereby reduce H_2S leak from the contactor. Simulation shows that H_2S leaks of below 1 ppmv can be achieved using only 5,000 ppmw of phosphoric acid and that even in Case 4, the H_2S leak is only 4 ppmv. Summary data are shown in Table 4.

Again it can be seen that using a stripping promoter provides a tremendous improvement in H_2S leak from the contactor, without significantly affecting the efficacy of Highsulf to produce a greatly improved SRU feed. The CO_2 slip, which is based on the external feed to the AGE unit, is extraordinarily high but quite consistent with the high H_2S content of the SRU feed stream. As long as the contactor remains lean-end pinched, phosphoric acid continues to provide great benefit; however, once the contactor become rich-end pinched no further benefit accrues. ■

Fig 4: **Dependence of H_2S leak on how vigorously Highsulf™ is applied**

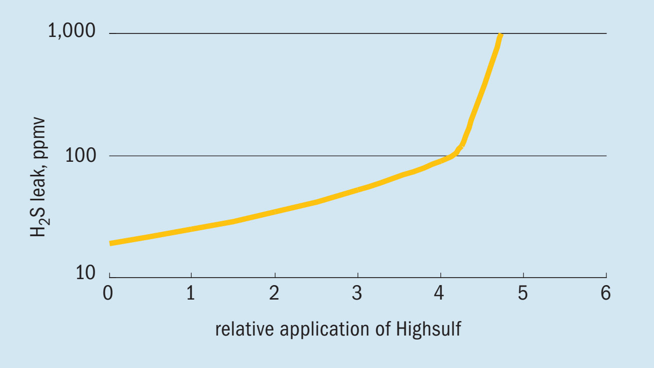
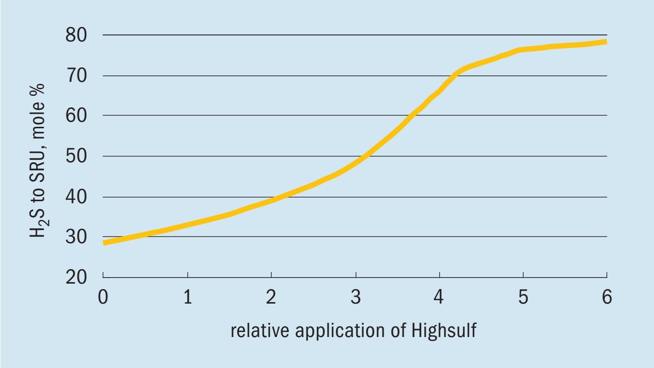


Fig 5: **Response of SRU feed quality to how energetically Highsulf™ is applied**



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