

Sulphide Absorbing Gas Cleaning In the Basics of Ethanolamines and Formaldehyde.

Z. F. Ismagilova, S. V. Mesheryakov.
J. P. Vasjko, F. R. Ismagilov.
Astrakhan State Technical University
Astrakhan, Russia

Raw material of heavy oil and gas deposits, developed in per Caspian lowland (Orenburg, Astrakhan, Tengiz, Zanazol), is characterized by high content of acid components (H_2S , CO_2) and sulphoorganic compounds. Under such circumstances the importance of industrial mining and development of new, economical and wasteless technologies, providing full and experienced usage of all raw compounds being developed, as well as growing ecological demands, acquire great significance.

Effective growth of traditional sulphide gas cleaning can be achieved by using different water or waterless absorbents in the basics of alkanolamines and compositional absorbents, for example, MDEA, glycols or their methyl ethers [1,2]. For small deposits and incidental oil gas cleaning, absorbing solutions, i.e. ethanol amine and formaldehyde mix, are of some interest [3]. Much of the very effective are the substances obtained as result of selective amine and formaldehyde synthesis in the presence of specially chosen catalysts [4, 5]. This method is interesting because sulphides obtained during sorbent and hydrogen sulphide interaction have many useful characteristics that can be applied in different industries and firstly in oil and gas industry. In its turn, this possibility allows to keep natural resources and reduce environmental pollution.

Comparative valuing of absorbent, i.e. different substances synthesized in the basics of amines and formaldehyde shows that ethanol amines are perspective base reagents. The experiments with monoethanolamines showed that hydrogen sulphide capacity was increasing with MEA and CH_2O , correlation growth, in favour of CH_2O . However, in correlations more than optimal (K_{opt}), the competitive reaction, leading to the formation of polymethylsulphide, begins. The reaction goes on until full consumption of formalin. Besides, there is the definite selective dependence of absorbents on hydrogen sulphide in the case-marked by perceptible qualities of carbon dioxide. Thus, the absorbent selectivity was tested by admitting carbon dioxide through absorbing solution (2 hours), and then hydrogen sulphide capacity was examined. The correlation data and fresh absorbent capacity indications are shown in table 1. In these experiments which lasted for an hour, 20% of absorbent solution was used, while hydrogen sulphide concentration made 30% cyc / e. The absorbents obtained by various correlations of initial reagents MEA to CH_2O were used in the presence of one and same catalyst. Cleaning rate control was performed with the help of the inert hydrogen sulphide analyzer "Riken Keiki" (Japan).

Table 1: Cleaning indexes and their dependence on absorbing conditions

Correlation MEA to CH_2O	6Kopt	3Kopt	1,5Kopt	Kopt	0,7Kopt	0,6Kopt
Residual concentration H_2S , mg / m ³	3	3	3	3	3	3
Selectivity H_2S	< 100	< 100	< 100	< 100	< 100	< 100

Table 2: Conditional Influence on hydrogensulphide gas cleaning effectiveness.

Temperature °C	0	20	50	95
Initial concentration H_2S , m	10	30	60	90

Rate Capacity, hour	120	240	450	1080
Residual concentration, H_2S , mg / m ³	3	3	3	3

When optimal absorbent content was obtained, laboratory rate cleaning, experiments with initial hydrogen sulphide concentration, gas rate and temperature supply, were done (table 2).

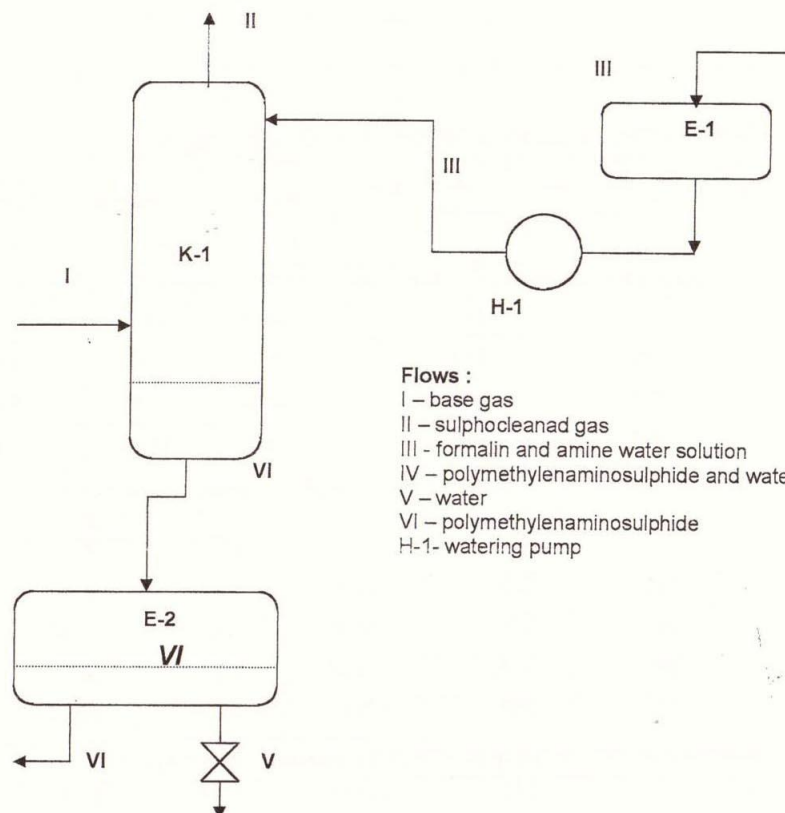
S_0 hydrogen sulphide gas cleaning is rapid and full, and it does not depend on temperature (for water solutions), pressure, hydrogen sulphide concentration and wide range of gas rates.

According to the result of the laboratory

experiments, the absorbent was recommended for experimental-industrial tests using hydrogen sulphide neutralization in oil, incidental and oxidized gas. The experimental absorbent production, with the output of 25 tons a day, was organized. The experimental physical and chemical characteristics of this reagent are given in table 3.

Table 3: New reagent physical and chemical characteristics.

Density at 20°C, g / m ³	1.085-1.096
Viscosity, sst (20°C)	3.7-6.3
Boiling temperature, °C	100
Class of danger	3 (moderately-toxic)
PH product	6-8
Stock temperature,	-20 -60
Air PDK, mg / m ³	0.5
Full hydrogen sulphide cleaning in 50% water solution correlation:	Hydrogen sulphide – absorbent –1 4



Pattern: principal scheme of the experimental installation for cleaning incidental gaseous from sulphides.

The technological adjusting of absorbent and incident of oil gas cleaning has begun. The definition of hydrogen sulphide in base and cleaned gas was made by the tetrametric metod [6]. Simalteneously absorbing temperature and gas flow dampness were controlled. Complete content of cleaned gas obtained by chromatographic method is shown in table 4.

Table 4: Chemical content of incidental oil gas.

N ₂	C ₁	CO ₂	C ₂	H ₂ S	O	C ₃	IC ₄	NC ₄	ΣC ₅
16,39	20,98	1,84	17,64	0,90	0,20	23,32	3,75	9,11	5,87

Table 5: Deep sulphocleaning dependence on absorption regime.

Test N	Consumption indexes		Content H ₂ S, g / 100 m ³		Cleanin Rate%
	Capacity rate, Per hour	Cleaned gas Quantity n m ³ / h	Base	Residual	
1.	2.	3.	4.	5.	6.
Absorbent Capacity-1 m ³ , temperature - 22-27 Pressure-0,45-55 kg / cm ²					
1.	115	239	230,11	3,44	98,5
	180	270	116,63	9,16	92,15
	270	540	102,69	10,8	89,48
	375	815	152,83	13,57	91,12
Absorbent Capacity-1 m ³ , temperature – 26,4-28,9 c, Pressure-0,79-1,2					

1.	2.	3.	4.	5.	6.
	145	220	147,72	5,24	96,45
	260	350	100,75	2,18	97,84
	380	1140	165,80	7,38	95,5
	450	750	171,6	33,0	80,77
Absorbent volume , temperature 21,9-28.2 c pressure 1,32-1,6 kg / cm ²					
3.	160	240	121,61	11,39	90,6
	255	380	100,45	10,53	89,52
	363	400	126,90	3,6	97,2
	500	650	149,3	2,3	98,46

Pressure influence of absorption on deep sulphocleaning is investigated at the interval of 0, 45-2, 75 kgs / cand gas flow rate from 100 to 535 nm³/h. The test results with the absorbent capacity loading-1 m³ are given in table 5. Gas dampness at the entry made 1, 17-17, 98 g / m³ and after the reactor-1, 64 + 12.68 g / m³.

Further tests were processed with absorbent volume loading-1,2m³, gas dampness-2,25-9,622 g / n m³ (entry) and 3,21-12,99 g / n m³ (exit) /

Table 6: Deep sulphocleaning dependence on absorption regime.

Test N	Expense indexes		Content H ₂ S, g / 100m ³		Cleaning rate
	Volume rate, per hour	Cleaned gas quantity, n m ³	Initial	Residual	%
1.	2.	3.	4.	5.	6.
Temperature 21,2-24,3 C, pressure 0,185-0,22 MPA					
1.	116,7	310			
	116,7	470			
	263,3	79			
	375,0				
Temperature 22,2-30,3 C, pressure 0,237-0,275 MPA					
2.	225	205	183,6	14,72	91,94
	225	420	140,96	10,46	92,58
	280	360	137,0	9,74	92,89
	302	405	137,0	9,74	92,89
	337,5				

It is seen from tables 4 and 5 that in all cases gas cleaning rate was rather high the expense for big absorbents is not calculated in these tests. It shows high absorbent sulphocapacity and proves the results of the laboratory experiments i.e. supplying hydrogen sulphide, gas through absorbing solution until it gives the product, containing sulphur and having polyminisulphide structure. This substance is being experimented now as corrosion inhibitor, biocide, and noble metals extragent. It can be used in many other interesting spheres as well.

This method may be useful for short tonnage local complexes of oil mining and processing, i.e. in places where traditional amine cleaning with the following producing of elementary sulphur using Claus's installations, is unreasonable, and unprofitable. This method is selective to hydrogen sulphide and inert to CO₂. Meanwhile it is effective concerning wide range of temperatures (from 0₀ C and more), pressure, gas flow rate, hydrogen sulphide concentration (from tracing to 100%). The latter are active to light merkaptans. When mining distant and dischargeable oil organo condensate deposits containing hydrogen sulphide and merkaptan, it is reasonable to use autonomous installations, consisting of two blocks: the producing block usually containing two liquids components and the neutralizing hydrogen sulphide block, working in the regime of barbotage gas processing.

References

- Alekseev S.Z., Afanasjev A.J., Kislenko N.N. Employment of new absorbents at gas processing plants. Gas Industry, 2000, N3, pp. 38-40
- Ismagilov F.R., Voltzov A.A., Safin R.R. et al. Ecology and new technologies in hydrogen sulphide gas cleaning, Ufa, Ecology, 2000, p. 214.
- Fahriev A.N., Fahriev R.A. / patent R F N 2121492, Claimed in 1996, 04. 11., published in 1998, 11. 10. Method of oil, gas condensate and their fractions cleaning off merkaptans and hydrogen sulphide.
- Ismagilov F.R., Vasjko J.P., Pivovarova N.A. et al. New approach to sulfohydrocarbon raw material. Gas industry, 2001, 11, p.-
- Ismagilov F.R., Safin R.R., Ismagilova Z.F. et al. Investigation of hydrogen sulphide absorbents in the basics of amines and formaldehyde. Works of the II International scientific conference "problems and perspectives of oil and gas developing industry in Kazakhstan in XXI century". - Aktau State University after Sh. Esenov, 2001, p.121-123.
- Vasilevskaya L.S., Shimko G.I., Ismagilov F.R. Book of methods defining concentration of polluting substances in industrial wastes. L. Hydrometizdat, 1987, p. 63-65.