PROCESS OF DIRECT CATALYTIC OXIDATION OF HYDROGEN SULFIDE TO ELEMENTAL SUFUR FOR PURIFICATION OF GAS STREAMS FORMED UPON HIGH-SULFUR CRUDE EXTRACTION AND PROCESSING

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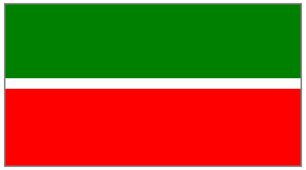

KAZAN

REPUBLIC OF TATARSTAN

FEBRUARY, 20-21

2006


St-Petersburg
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HYDROGEN SULFIDE EMISSIONS UPON EXTRACTING AND PROCESSING OF HIGH-SULFUR CRUDE IN REPUBLIC OF TATARSTAN

Oil-associated gases

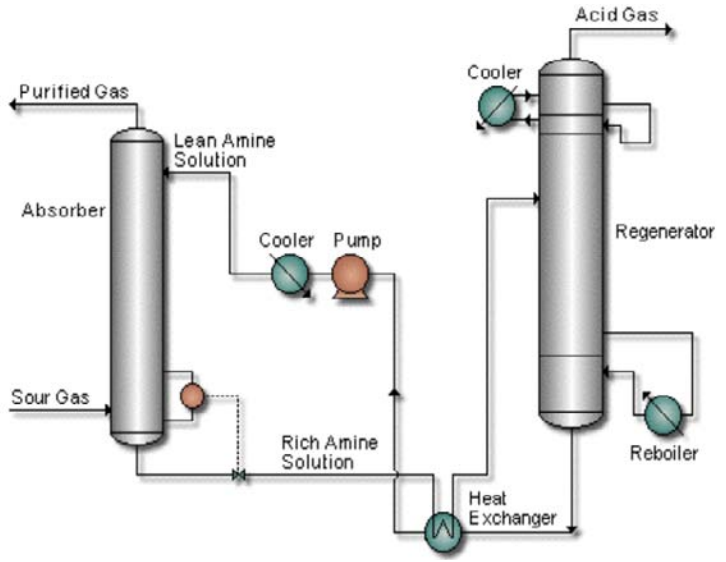
Total amount in Republic of Tatarstan up to billion nm^3 per year. H_2S content – 1.5 % vol. (average)

Hydrodesulfurization (HDS) of oil fractions at refineries

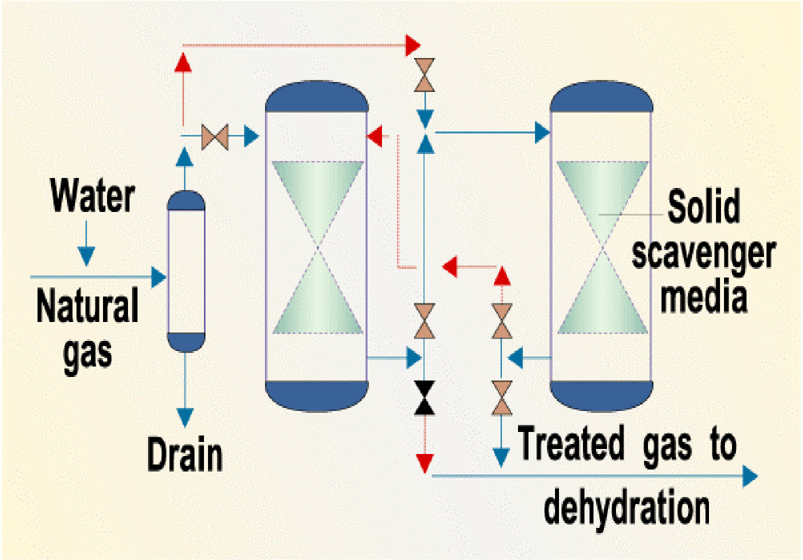
Total amount in Republic of Tatarstan up to 200 millions nm^3 per year

Pokonova Yu. *Neft` i nefteprodukty. Handbook, Moscow, 2003.*

ADSORPTIVE METHODS OF GASEOUS STREAMS PURIFICATION FROM HYDROGEN SULFIDE



Gas stream purification from H_2S with amine solution



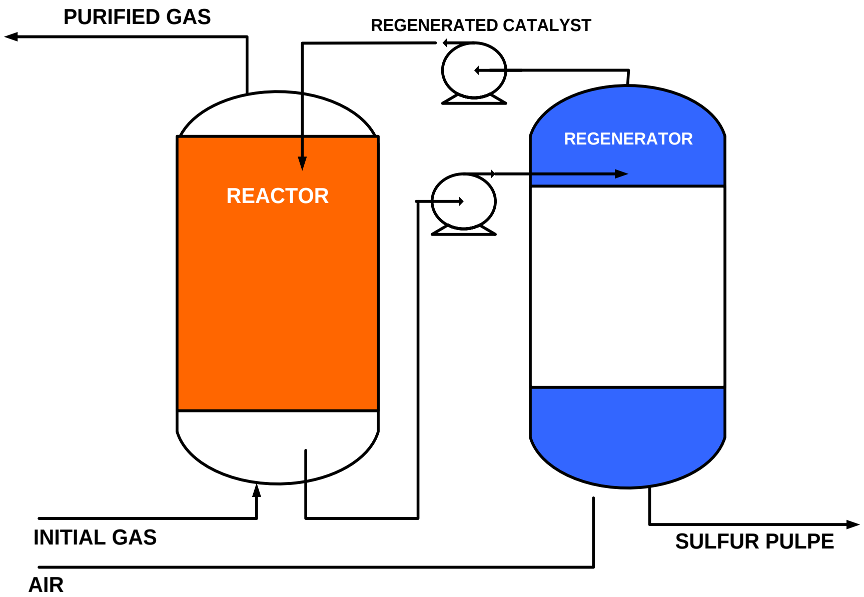
Gas stream purification from H_2S with solid sorbents

COMMON DRAWBACKS

- **A methods for only isolations of acid components (H_2S and CO_2) from purified gas;**
- **The processes are noncontinuous (adsorption-regeneration steps);**
- **In use only in combination with the subsequent hydrogen sulfide processing technology e.g. Claus process;**

HOMOGENEOUS DIRECT OXIDATION HYDROGEN SULFIDE TO ELEMENTARY SULFUR

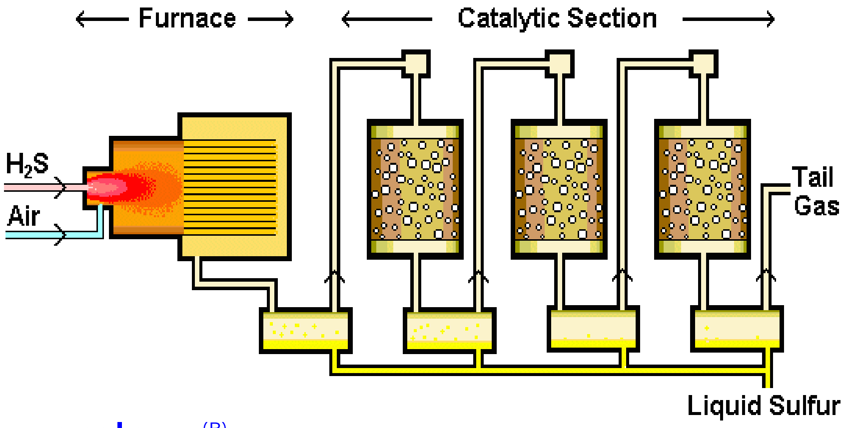
The examples of the commercially available processes:
ARI - Lo-Cat I®, ARI - Lo-Cat-II® by Wheelabrator Clean Air Systems, Inc.
SulFerox® by Shell



DRAWBACKS

The process is non-continuous (the oxidation and regeneration steps)
High corrosion of equipment because of sulfuric acid formation
Use of liquid reagents

HETEROGENEOUS OXIDATION OF HYDROGEN SULFIDE WITH SULFUR DIOXIDE (CLAUS PROCESS)



Modifications: Superclaus® COPE®

DISADVANTAGES

- The process is consisted of several stages;
- Deactivation of the catalyst due to coke formation or sulfidation;
- Need additional technological processes of tail gas purification;
- Emissions of toxic secondary side products such as COS, CS_2, sulfuric acid, carbon monoxide, nitrogen oxides;
- Difficult to build and operate small capacity units.

DIRECT OXIDATION OF HYDROGEN SULFIDE

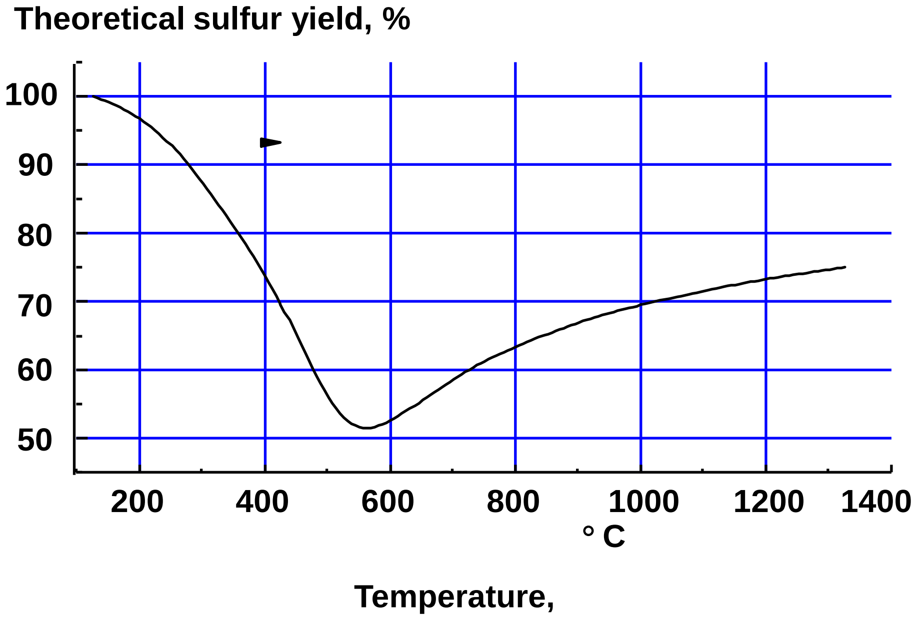
MAIN REACTION

$$n\,H_2S + n/2\,O_2 \Rightarrow S_n + n\,H_2O + Q \quad (1)$$

SIDE REACTIONS

$$H_2S + 3/2\,O_2 \Rightarrow SO_2 + H_2O$$

$$2\,H_2S + SO_2 \Rightarrow 3S + 2\,H_2O$$



Gamson B.W., Elkins R.H. // Chemical Engineering Progress, 49, 1953, pp.203-215.

MAIN ADVANTAGES OF DIRECT OXIDATION OF HYDROGEN SULFIDE PROCESS

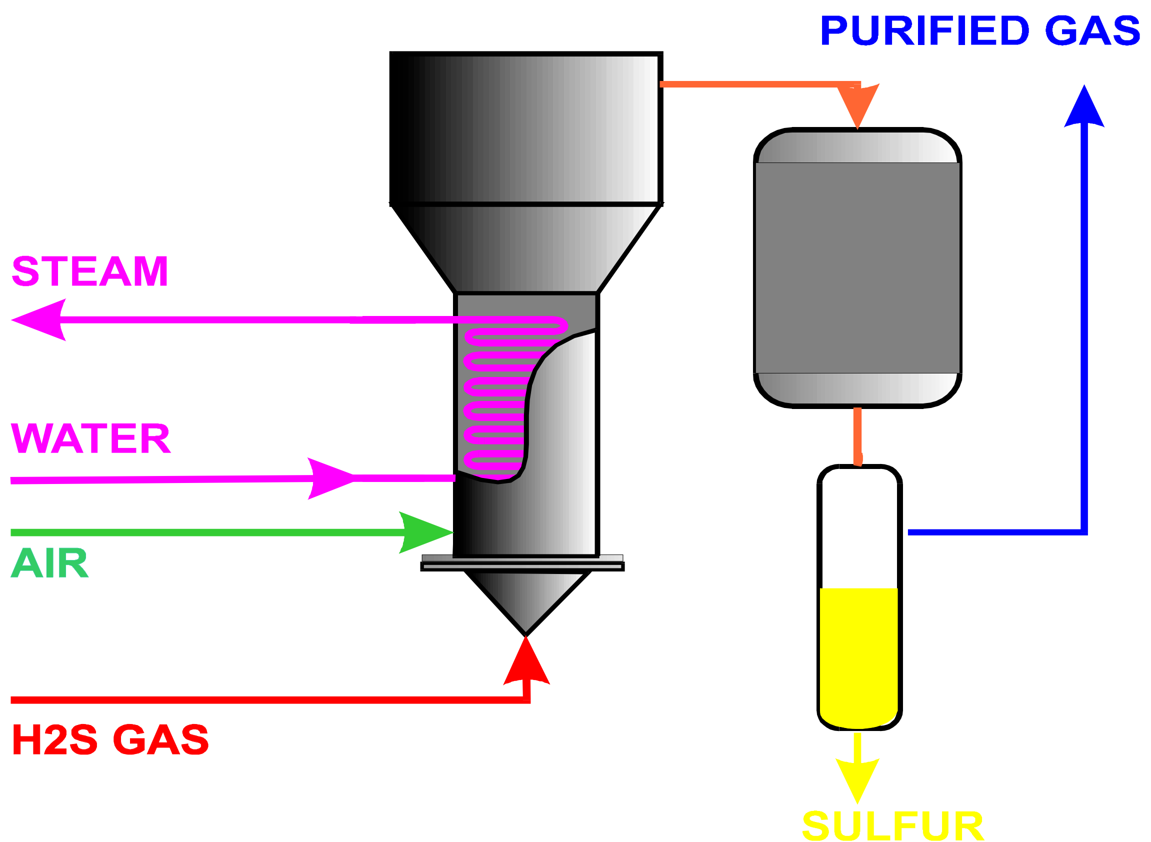
- **One catalytic reactor allows attaining of H_2S conversion of up to 98%;**

- **"Soft" reaction conditions (T=220-280^oC) allow selective oxidation of H_2S in it's presence in the mixture with hydrocarbons;**

- **Possibility to build and operate units of small and medium size.**

However, since reaction (1) is highly exothermic (ΔH= -221 kJ/mole) technological problems of efficient heat removal from a fixed catalyst bed limit the application of this technology to gas streams with H_2S concentration higher than 10 vol.%.

DIRECT SELECTIVE OXIDATION OF HYDROGEN SULFIDE IN REACTOR WITH FLUDIZED BED OF CATALYST



Purification of highly concentrated streams, such as "acid", natural and hydrorefining gases. There are no restrictions on H_2S concentration in initial gases. (Смотреть)

- Ismagilov Z.R., Zamaraev K.I., Khairulin S.R. et al. *US Patent No 4.886.649 (1989).*
- Ismagilov Z.R. et al. Russiann Refiner tests new One-Stage H_2S Removal Process. *Oil & Gas Journal, 1994. March, pp.81-82*

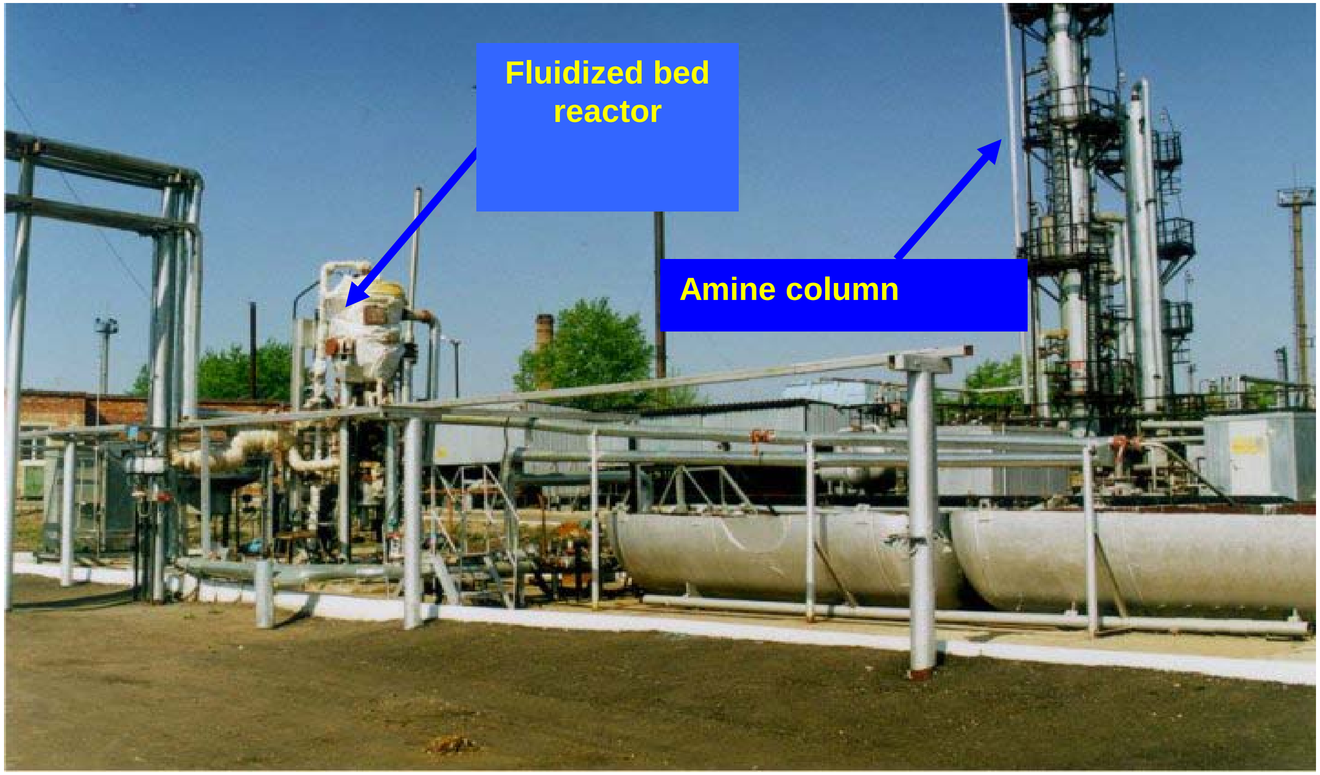
BACKGROUND OF THE PROJECT DEVELOPMENT WITH FLUDIZED BED REACTOR

Place Object	Operation conditions a) scale b) gas supply	Year	Hydrogen sulfide removal efficiency, %
Astrakhan natural gas $C(H_2S)$-27 vol.%	pilot up to 50 nm^3/h	1987	98
Astrakhan natural gas $C(H_2S)$-27 vol.%	pilot up to 50nm^3/h	1988	98
Astrakhan natural gas $C(H_2S)$-27 vol.%	pilot up to 20nm^3/h	1991	98
Ufa Refinery hydrodesulfu- rization gas $C(H_2S)$-70% vol..	pilot up to 50 nm^3/h	1990	98

FLUIDIZED BED REACTOR

Place Object	Operation conditions a) scale b) gas supply	Year	Hydrogen sulfide removal efficiency, %
Shkapovo GPP(*) acid gas C(H_2S)-65% vol	semi-industrial up to 350 nm3 /h	1995	98
Bavly oil field acid gas C(H_2S)-50% vol	semi-industrial up to 50 nm3 /h	2005	99

GPP – gas processing plant



The Claus process replacement
(Bavly high-sulfur crud deposit at Republic of Tatarstan)

Industrial plant (reactor with fluidized bed of granulated catalyst).

Field proven efficiency of H_2S removal > 99%.

REACTOR WITH FLUIDIZED BED OF GRANULATED CATALYST

(BAVLY CRUD DEPOSIT AT REPUBLIC OF TATARSTAN)

ANALYSIS OF TAIL GASES OF INDUSTRIAL PLANT
(Bavly)

ДЕК. 26 2005 13:38 СТ (analysis certificate)

№	Компоненты	Формула	Концентрация объёмная % об.
1	Углекислый газ	CO_2	33,85
2	Кислород	O_2	0,43
3	Азот	N_2	64,45
4	Сероводород	H_2S	0,29
5	Метан	CH_4	0,00
6	Этан	C_2H_6	0,14
7	Пропан	C_3H_8	0,54
8	изо-Бутан	$i\text{-}C_4H_{10}$	0,05
9	н-Бутан	$n\text{-}C_4H_{10}$	0,14
10	изо-Пентан	$i\text{-}C_5H_{12}$	0,05
11	н-Пентан	$n\text{-}C_5H_{12}$	0,06
12	Гексан	C_6H_{14}	0,00
	Сумма		100,0

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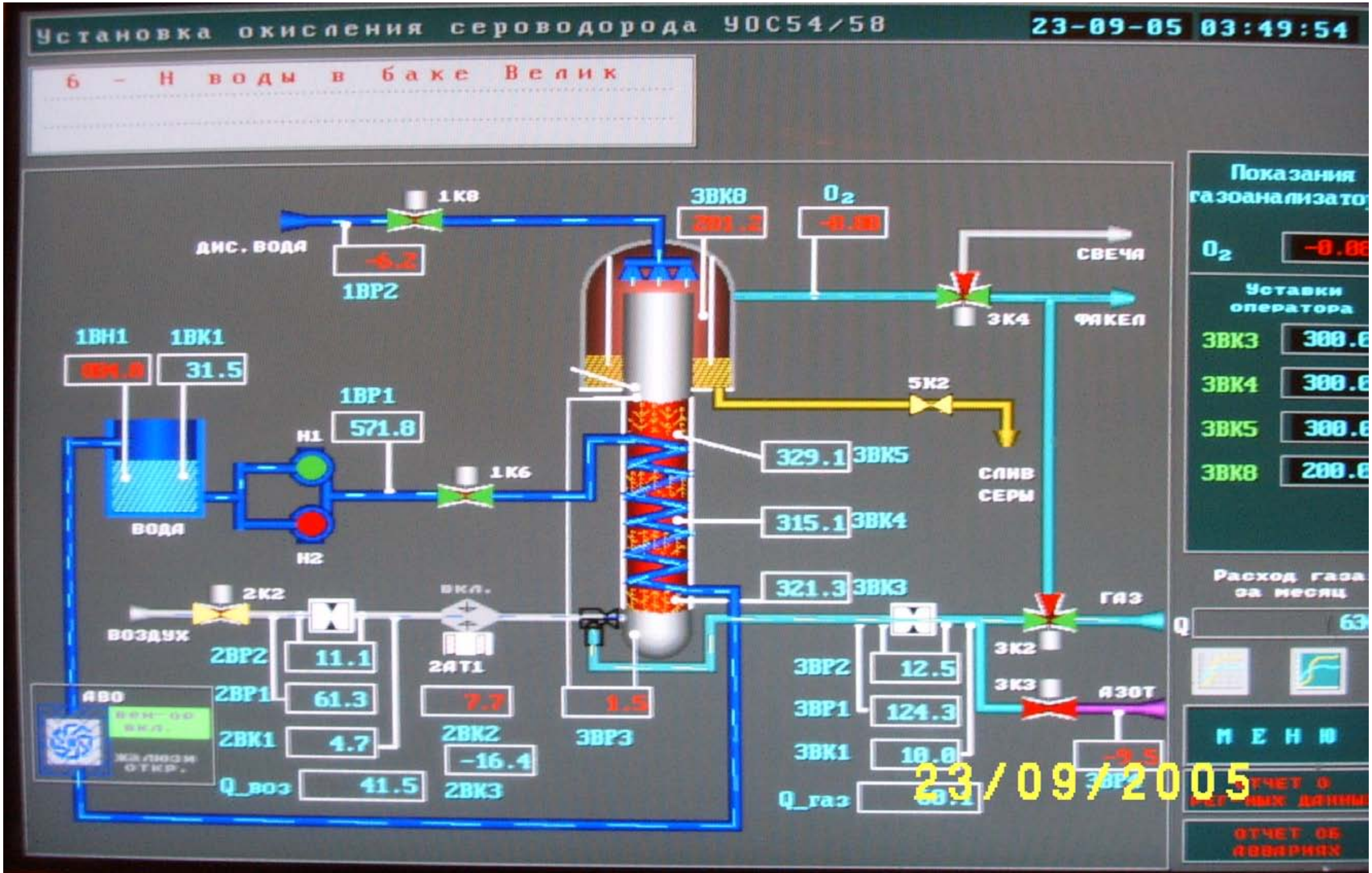
Аттестат аккредитации № РОСС RU.0001 613484 от 27.09.2002

Зав. лабораторией ________ Ермолаева А.

Hydrogen Sulfide Content in Initial Acid Gas- **54% vol.**

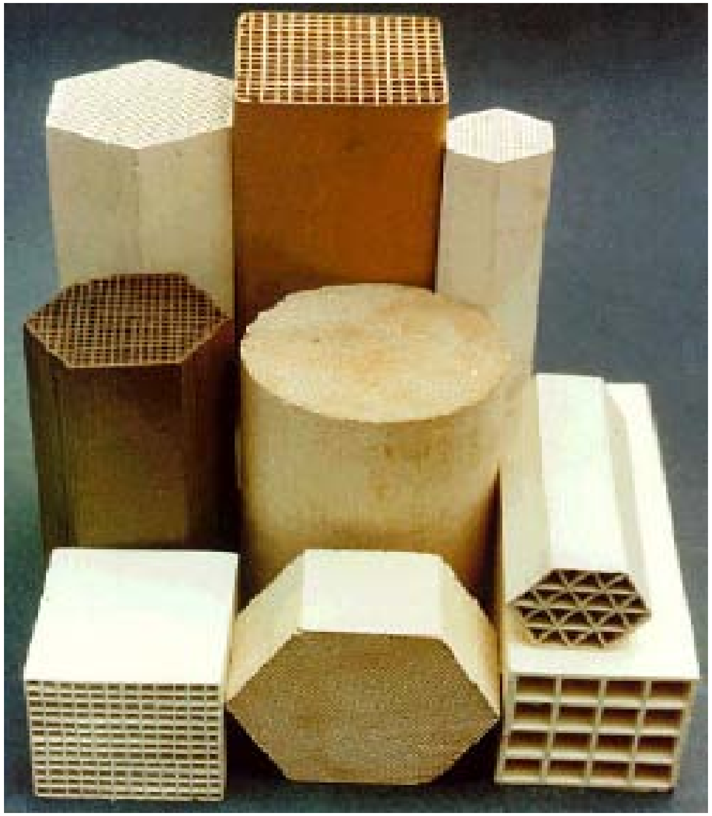
Sulfur Yield – **99.5%**

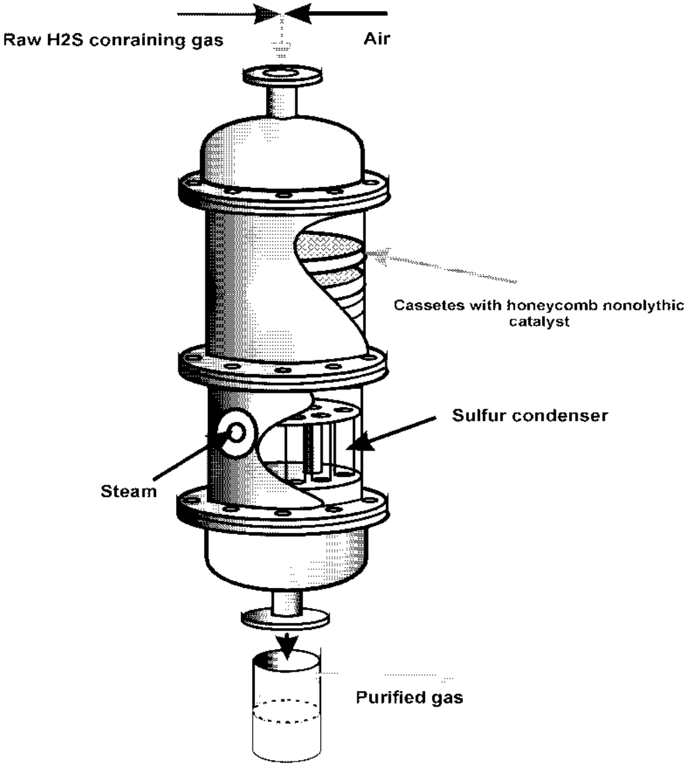
SCREEN SHOT OF THE COMPUTATIONAL PROCESS CONTROL



DIRECT SELECTIVE OXIDATION OF HYDROGEN SULFIDE IN REACTOR WITH HONEYCOMB MONOLYTHIC CATALYST

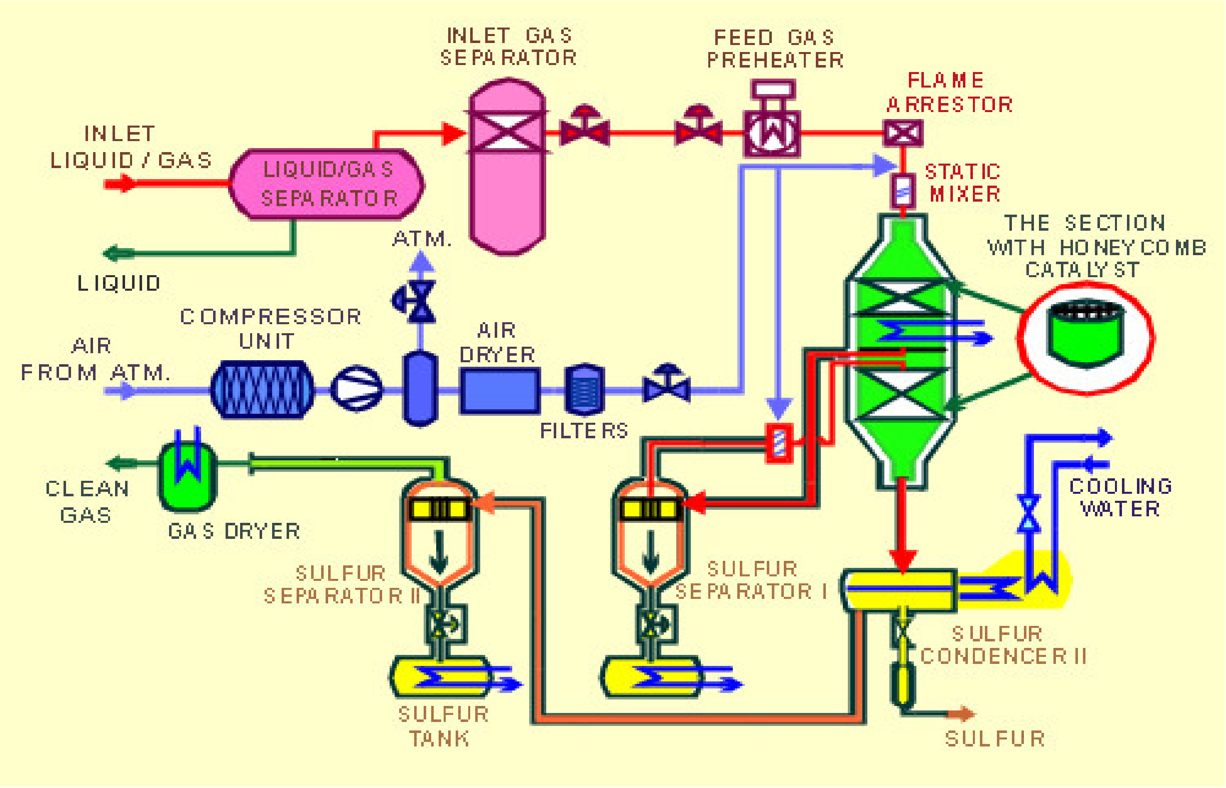
Purification of oil-associated gases, tail-gases, bio-gas, geothermal steam



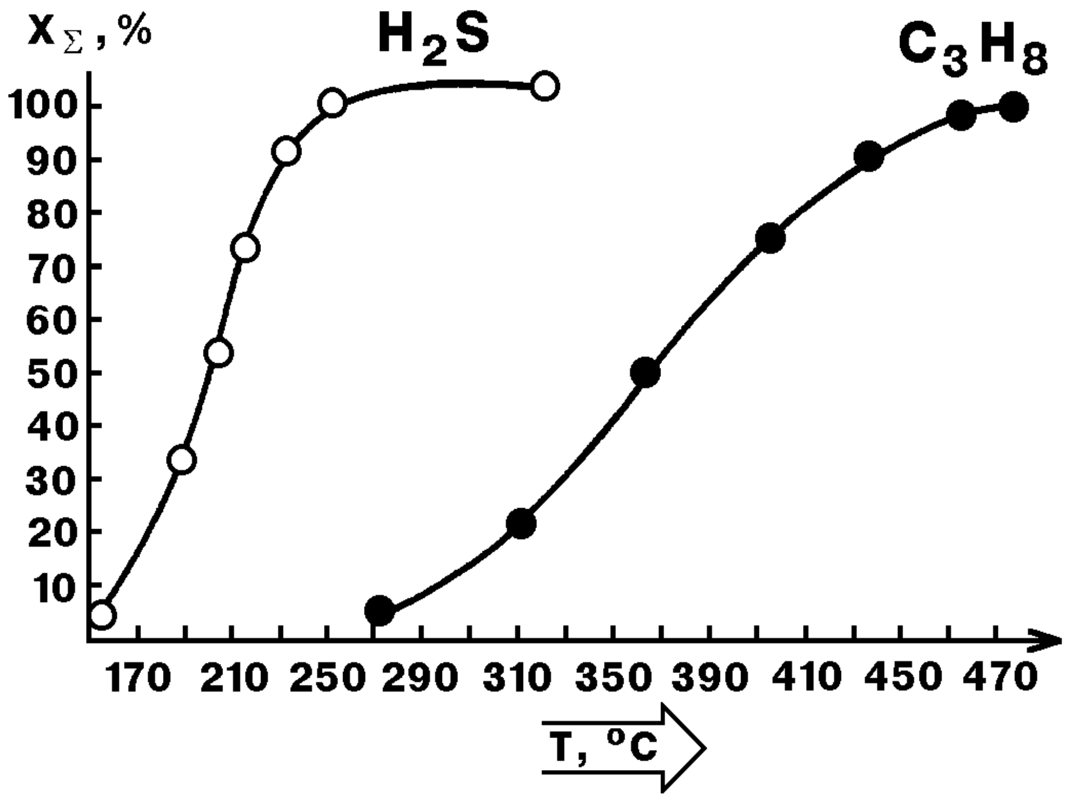


Ismagilov Z.R., Kerzhentsev M.A., Khairulin S.R. et al., *Hydrocarbon Technology International, Quarterly, Winter Issue 1994/1995, pp.59-64.*

This process modification can be used for efficient removing H_2S directly from the oil-associated gas streams. Depending on the desired level of H_2S removal and project economics, the treated gas may be used as an onsite fuel to power fired heater equipment, compressors, power generation, or be marketed for sale



CATALYTIC OXIDATION OF H_2S IN PRESENCE OF PROPANE



catalyst	- $MgCr_2O_4/\gamma$ - Al_2O_3
residence time	- 0.8 s
C_{H2S}	- 30 vol.%
C_{C3H8}	- 15 vol.%

BACKGROUND OF THE PROJECT DEVELOPMENT WITH HONEYCOMB MONOLYTH REACTOR

Place **Object**	**Operation conditions** **a) scale** **c) gas supply** **d) operation pressure**	**Year**	**Hydrogen sulfide removal efficiency, %**
Ufa Refinery tail gas of Claus process $C(H_2S)$-2% vol..	fixed bed pilot up to 20 nm3 /h pressure - atm.	1989-1990	**98**
Kamchatka peninsula geothermal steam $C(H_2S) < 1\%$ vol $C(H_2O) > 99\%$	pilot up to 0.5 tn. steam/h P up to 1.0 MPa	1989-1990	**99.9** **2500h of continuous work**
Astrakhan GPP(*) tail gases of Claus process $C(H_2S)$- 2 vol.%	pilot up to 20 nm^3 /h pressure - atm.	1989-1990	**98**

HONEYCOMB MONOLYTH REACTORS

Place Object	Operation conditions a) scale c) gas supply d) operation pressure	Year	Hydrogen sulfide removal efficiency, %
Orenburg GPP gases of zeolites regeneration $C(H_2S)$- 2 vol.% C(RSH)- 5% vol	up to 20 nm^3/h pressure up to 5.0 MPa	1990	98
Novo-Ufimsky Refinery tail gas of Claus process $C(H_2S)$- 2% vol	semi-industrial 7000 nm^3/h	1994	98

SEMI-INDUSTRIAL UNIT FOR PURIFICATION OF CLAUS PROCESS TAIL GAS

CAPACITY UP TO 7000 nm^3/hour

SUMMARIZED ADVANTAGES OF THE BIC TECHNOLOGIES

1. The creation of compact, highly efficient, one-stage units that can be mounted:
- On-site for direct purification of oil associated gas;
- On site for treatment of sour gas after amine unites;
- At refineries and gas processing plants as alternative to the Claus sulfur recovery units.

2. The substantial improvement of environment, due to excluding of hazardous emissions and wastes.

3. Production of the fuel gas and elemental sulfur of high purity.

4. Diminishment of the capital outlays (in comparison with Claus units 3-4 times).

5. Diminishment of the service costs (in comparison with Claus units 4-5 times).

The payback period for the direct oxidation units – 0.5-1.5 years.

OUR PARTNERS:

Joint-Stock Company “VNIIUS”

- ***Process design***

Joint-Stock Company “TATNEFT”

- ***Oil-associated gas purification***

Joint-Stock Company “Tatneftekhiminvest-holding”

- ***Technology implementation in Republic of Tatarstan***

The Russian Joint-Stock Company “Gazprom”

- ***Natural gas purification***

Joint-Stock Company “Bashnefekhim”

- ***Hydrodesulfurization gases purification at refineries***

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