velopment of Processes for Purification
Coal Processing Gases from Sulphur and Cyan
the Application in Energy Technologies

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tract

or the efficient use of gases formed in a number of thermochemical procedures of carbon processing
cessary to purify them from hazardous impurities, such as H_2S, HCN, NH_3, resinous substances
fy the gases, it is proposed to use the liquid catalytic procedure with the soluble derivatives of co
alocyanine as a catalyst. This method allows achieving the required purification extent with low expe
purified gases can be used to obtain electricity and heat, and also as chemical raw material for obtai
onia, methanol, liquid fuel, *etc*. Elemental sulphur is obtained as a result of purification.

DUCTION

normous resource basis of the coal indus-
of Russia (the first place in the world
respect to coal resources and the third
e in the explored resources) allows one to
d a long-term concept of the develop-
t of economical coal power engineering
nd coal processing into chemical products.
rmochemical coal processing (coking, low-
perature coking, semi-coking, gasification,
m and oxygen conversion) results in the
ation of the corresponding gases which
r purification from hazardous impurities
be used as a fuel or as a raw material for
ining chemical products (ammonia, meth-
, liquid fuel, *etc*.). The fraction of coal
ected to gasification is likely to increase
tially during the nearest years with the

OUTLOOKS OF COAL PROCESSING BY MEANS
OF PRELIMINARY GASIFICATION FOLLOWED
BY THE PURIFICATION OF THE RESULTING GAS

One of the promising methods of
processing into electric and thermal energy
volves preliminary gasification of the coal
lowed by purification of the resulting gas f
hazardous impurities (sulphurous, nitrogen-
taining compounds, gum-like products, s
particles). The advantage of this technolog
carbon processing (gasification + purifica
of the resulting gas) is the possibility of inc
ration of the purified gas in gas turbine po
plants (GTPP) which allow transforming u
28−32 % of the heat of burnt fuel into el
ricity [2]. Incineration in GTPP equipped v
boiler-utilizers helps achieving also max
total utilization of the heat of burnt fuel

...e gas till a point below dew point for sul-
..ric acid, since the waste gas does not con-
.. sulphur oxides. The flue gas will contain
..olid particles, sulphur or nitrogen oxides.
.. absence of nitrogen oxides in exhaust gas-
.. is achieved thanks to preliminary purifica-
.. of the gas from nitrogen-containing com-
..nds. In addition, temperature not higher
.. 1500 °C is maintained in the combustion
..mber of GTPP, which prevents the for-
..ion of noticeable amounts of nitrogen oxi-
.. from nitrogen and oxygen. Such a low tem-
..ture of incineration of the gas obtained
.. coal gasification, unlike natural gas incine-
..on, is possible due to its high hydrogen
..ent.

.. addition to high extent of utilization of
.. heat of burnt fuel (processed coal) and
..ronmental safety, this technology has one
..e important advantage. Coal gasification and
..neration of the obtained gas can be per-
..ed in different territories: gasification can
..arried out close to coal mining or unload-
..site, and incineration close to the site where
.. electricity and thermal energy are to be
..umed. Transportation of the obtained gas
..g pipeline is possible due to its prelimi-
.. purification from hazardous (aggressive)
..ixtures.

..he application of this technology of coal
..essing into electricity and thermal energy
.. very urgent nowadays. Because of increas-
.. difficulties in oil and gas production and
.. limited resources (it is assumed that the
..urces of natural gas in Russia will be over
.. the nearest 30−40 years), a substantial
..ease in the fraction of coal in the total
..unt of fuel to be processed into electricity
.. thermal energy is planned [1]. At the con-
..ation of the existing technologies, growth
.. coal processing will cause a substantial in-
..se in emissions into the atmosphere. Ac-
..ng to the data of RAO "UES of Russia",
..ncrease in NO_x emission by 13 %, SO_x by

..or of about 4.

In order to obtain electricity and ther..
energy with the help of gas turbine po..
plants equipped with boiler-utilizers, one ..
also use gases obtained by coking, semi-..
ing, steam and oxygen conversion of coal. ..
thods are also developed to use poor gas f..
coal gasification in the existing and spec..
developed GTPP, including those with the c..
lytic combustion chambers. This will allow ..
to process wastes from coal-concentrating pl..
into electricity and thermal energy. The us..
the resulting coal wastes (high-ash coal) for ..
erating electric and thermal energy would ..
low one to save coal resources not mined ..
prevent land disabling by tailings (coal was..
In addition, one cannot exclude the possib..
to use coal wastes accumulated previously (t..
may account for millions tons near actua..
previously existing coal concentrating plan..

The major hazardous components in coal ..
cessing gases are hydrogen sulphide (H_2S), ..
monia (NH_3) and hydrogen cyanide (H..
which cause the corrosion of equipment ..
ing transportation, compression and comb..
tion. Gases obtained by thermochemical ..
processing can be used as chemical raw m..
rial or as fuel. H_2S and HCN are the stron..
catalyst poisons in the synthesis of ammo..
methanol and liquid fuel. During combus..
of coal processing gases, these compounds ..
transformed into not less toxic sulphur and ..
rogen oxides.

Amine purification has become the m..
widespread method of fuel gas purifica..
from H_2S, followed by the processing of ..
sulting acidic gases into elemental sulphur ..
cording to Claus procedure. However, the ..
plication of amine methods to purificatio..
gases obtained by coal processing is hinde..
due to the presence of such compounds as H..
resins, easily polymerized unsaturated hy..
carbons, nitrogen bases (NH_3), solid part..
(ash, coal) [5]. The presence of the listed ..

...tion process (amine purification + utiliza...
of acidic gases according to Claus proce-
...e) also worsen in the case when installa-
...s with low productivity with respect to the
...acted H_2S are built, for example, for the
...ification of low-sulphur gases. In this case,
...zation of a substantial part of heat during
...combustion of acidic gases at the stage of
...r processing according to Claus procedure
...impossible. Because of the presence of res-
...ke and easily polymerized components in
...gas obtained by carbon gasification, the
...ication of adsorption and heterogeneous
...lytic high-temperature purification proce-
...es is also hindered.

...n order to purify gases obtained by ther-
...hemical coal processing, the methods of
...ification from sulphur and sulphur-cyan pu-
...ation existing at present or being under de-
...pment can be recommended, since they
... into account that the gas under purifica-
...contains HCN, NH_3, unsaturated hydrocar-
...s, resin-like compounds in addition to H_2S.
...n the world industry, more than fifteen
...ions of technological processes of coke gas
...ification have been introduced [6, 7]. Such
...versity is due to the differences in the com-
...tion of coked mixtures and therefore in
...composition of the coke gas, and also due
...ifferent requirements to purification ex-
... and to resulting products. Oxidative puri-
...ion methods involving liquids (wet proce-
...es) are widespread. The processes of wet
...ative sulphur- and cyan purification (Hol-
...-Stretford, Fumax-Rodax, Takahacs-Hai-
...x) providing high degree of gas purifica-
... from H_2S and HCN (up to 99.9 %) [4] are
...t widespread in Japan, Great Britain and
...ada. The essence of these processes is re-
...ed to the absorption of acidic components
...oke gas by ammonia or soda solution. After
..., catalytic oxidation of the absorbed hyd-
...n sulphide to sulphur is performed in so-
...n, and the catalyst is recovered by blow-
...ir through the solution. The processes are

are preliminarily purified from resinous s...
stances and from hydrogen cyanide. For h...
sulphur gases obtained by coal processing, ...
liminary purification from HCN is economi...
ly efficient, because large amount of comm...
cial high-quality sulphur is obtained as a re...
of subsequent purification of gas from ...
The resulting water-wetted sulphur can be ...
as a fungicide [7].

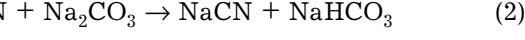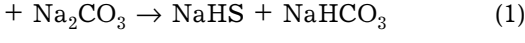## DEVELOPMENT OF PROCESSES FOR THE PURIFICAT...
OF COAL PROCESSING GASES

A specific feature of gases obtained by t...
mochemical processing of eastern coal is ...
content of sulphurous compounds (H_2S) ...
as a consequence, low H_2S/HCN ratio ti...
H_2S/HCN = 1, which makes it economi...
unreasonable to purify the gas separately: f...
from HCN, and then from H_2S. It is desir...
to perform simultaneous purification of s...
gases from hydrogen sulphide and from h...
rogen cyanide obtaining thiocyanates. In o...
to avoid accumulation of these salts in s...
tion, either intensive drainage or frequent...
placement of absorbing solution is necess...
so the absorbing solution should be rather ch...
Requirements to the level of admixture...
gas, which are able to get accumulated in ...
absorbing solution, can be made not so ...
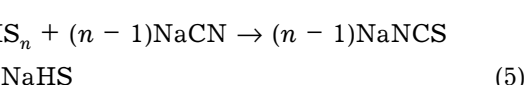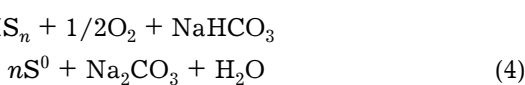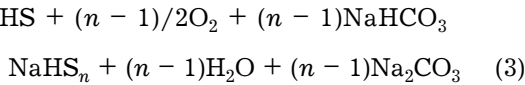because absorbing solution will be often...
placed.

For low-sulphur coke gas, a catalytic liq...
oxidative method of simultaneous purifica...
from H_2S, HCN and resin-like substances...
been proposed, with soluble derivative...
cobalt phthalocyanine (CoPc) as a catalys...
9]. Cobalt phthalocyanine and its water-sol...
derivatives are characterized by high acti...
in liquid-phase oxidation of hydrogen sulp...
by oxygen in alkaline medium. Due to ...
activity, the concentration of phthalocya...
catalysts in absorbing solutions can be very...
(several milligrams per litre), which prov...

...containing an alkaline reagent (Na_2CO_3 ... NH_4OH) and a catalyst, which is a soluble phthalocyanine derivative in monomeric [9] or ...meric form [8]; this results in absorption ...hazardous admixtures: H_2S, HCN and resi... substances. The saturated absorbing solu... is then blown with air at the regeneration ...e; this is accompanied with catalytic oxida... of the absorbed hydrogen sulphide, which ...resent in solution mainly in the form of ... ions, by the dissolved oxygen. As a result ...oxidation, depending on conditions, diffe... products can be formed: elemental sul..., thiosulphates, sulphites, sulphates [10, ... During the simultaneous purification of the ...from H_2S and HCN, it is necessary to ob... elemental sulphur along with thiocyanates. ...intermediate product of the oxidation of ... ions to sulphur is polysulphide ion. The ...ence of freshly formed elemental sulphur ... polysulphide ions in solution allows hyd... n cyanide absorbed from gas to be trans...ed rather rapidly into thiocyanates [12]. ... following reactions proceed under the op...l mode of the process of simultaneous pu...ation of gas from H_2S, HCN and resinous ...stances:

...t absorption stage

$$... + Na_2CO_3 \rightarrow NaHS + NaHCO_3 \tag{1}$$

$$...N + Na_2CO_3 \rightarrow NaCN + NaHCO_3 \tag{2}$$

...t regeneration stage

$$...HS + (n-1)/2O_2 + (n-1)NaHCO_3$$
$$... NaHS_n + (n-1)H_2O + (n-1)Na_2CO_3 \tag{3}$$

$$...S_n + 1/2O_2 + NaHCO_3$$
$$... nS^0 + Na_2CO_3 + H_2O \tag{4}$$

$$...S_n + (n-1)NaCN \rightarrow (n-1)NaNCS$$
$$... NaHS \tag{5}$$

...fication results in the formation of thiocya...es and elemental sulphur. The worked out ...tion is processed to obtain H_2S, which is

phase oxidative purification of low-sulphur ... gas from sulphur and cyan were mastered u... tetrasodium salt of 2, 9, 16, 23-tetrasul... nate of cobalt phthalocyanine (CoTSP), ... of highly active and best investigated sol... derivatives of phthalocyanine, as a cata... [10, 11, 13−16].

The available literature data and our ... results obtained in the investigation of ... mechanism of the catalytic action of Co... in liquid-phase oxidation of hydrogen sulp... by oxygen [10, 11, 13−18] allowed us to es... lish the main parameters of the oxidatio... absorbed hydrogen sulphide at the stag... oxidative regeneration (pH, composition of ... absorbing solution, catalyst concentration).

Selection of optimal pH of absorbing solutio...

The following guidelines were followed w... choosing the optimal pH of solution:

1. High yield of sulphur as a result of ... oxidation of HS^- ions by oxygen is obser... as a result of the oxidative-reductive tr... formation of the catalyst: $[Co(II)TSP]$ ... $[Co(I)TSP)]_2$ [15]. In the case of the forma... of complexes of the catalyst with oxygen ... CoTSP and $[O_2 \; CoTSP \; O_2]$ [16], prevailing ... mation of oxygenated sulphur compounds (... phites, sulphates) is observed during the ... dation of HS^- ions. An increase in pH of s... tion helps stabilizing the oxygen complexe... CoTSP [17] thus decreasing the yield of ... mental sulphur and increasing the yiel... oxygenated sulphur compounds.

2. With an increase in pH of solution, ... rate of non-catalytic oxidation of polysulp... formed according to reaction (3) increases ... stead of reaction (4), oxidation of polysulp... ions by oxygen proceeds with the forma... of sulphites and sulphates.

3. At pH $> 9−10$, disproportionation of ... formed elemental sulphur is observed:

...oxidation of HS⁻ ions, which, in turn, en... s high extent of gas purification from HCN ...t the formation of thiocyanates. On the other ...d, a decrease in pH can sharply decrease ...sulphur-absorbing capacity of the absorb-...solution. Because of this, it is necessary to ...ose optimal pH.

...ction of optimal composition
...e absorbing solution
...methods to maintain this composition

...When choosing optimal composition of the ...orbing solution, we took into account the ...ct of different compounds present in solu-...on the activity and selectivity of the CoTSP ...alyst toward sulphur in the liquid-phase ...ation of hydrogen sulphide.

...he absorbing solution can contain either ...compounds absorbed from the coke gas or ...compounds that are formed during purifi-...on from sulphur and cyan, and accumulat-...the absorbing solution. In addition to the ...alyst and alkaline agent, the absorbing so-...on contains the captured hydrogen sulphide ...⁻) and hydrogen cyanide (CN⁻), freshly ...ed elemental orthorhombic sulphur, thio-...hate, sulphite, sulphate and thiocyanate ...odium (ammonium). The effect of all these ...pounds on the catalytic liquid-phase oxi-...on of hydrogen cyanide in the presence ...oTSP was studied in [19−22]:
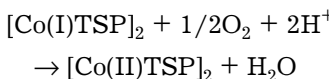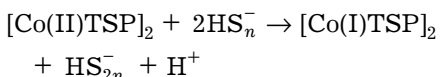
...) The presence of elemental sulphur and ...sulphates helps increasing the yield of sul-...r as a result of oxidation [22];

...) Thiocyanates and sulphates have only a ...k effect on the properties of CoTSP cata-...[22];

...) Sulphite and cyanide ions are strong in-...tors [20−22].

...he activity of the CoTSP catalyst and its ...ctivity toward sulphur decrease sharply in ...presence of sulphite and cyanide ions. Their ...on is due to rapid reactions:

HS⁻ ions by oxygen according to the poly-
phide mechanism. Not a slow reaction betw
the catalyst and HS⁻ ions occurs during
process but a rapid interaction of the cata
with HS_n^- ions:

$$[Co(II)TSP]_2 + 2HS_n^- \rightarrow [Co(I)TSP]_2 + HS_{2n}^- + H^+$$

$$HS_{2n}^- + HS^- \leftrightarrow HS_n^- + HS_{n+1}^-$$

$$[Co(I)TSP]_2 + 1/2O_2 + 2H^+ \rightarrow [Co(II)TSP]_2 + H_2O$$

Realization of the polysulphide mechanism
lows conducting the oxidation of HS_n^- ion
oxygen at a high rate and high sulphur yi

Cyanide ions not only destroy polysulph
but also directly affect the catalyst causing
bilization of the oxygen complexes [23]
promoting slower and deeper oxidation of
ions by oxygen, which results in the forma
of oxygenated sulphur compounds: sulp
and sulphate [11].

The method of simultaneous purificatio
low-sulphur coke gas from H_2S and HCN u
a soluble derivative of cobalt phthalocya
as a catalyst provides limitation of the a
mulation of sulphite and cyanide ions in
sorbing solution. Concentrations of SO_3^{2-}
CN^- ions should be rather low, so that
following relations between the concentrat
of HS^-, SO_3^{2-} and CN^- ions in the solu
entering the stage of oxidative regenera
should be fulfilled:

$$[HS^-]/[SO_3^{2-}] > 8-10; [HS^-]/[CN^-] > 15-20$$
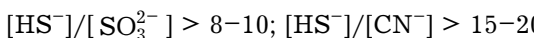
Low concentration of sodium (ammoni
sulphite is maintained in the absorbing s
tion due to the presence of suspended fre
formed elemental sulphur (1−5 g/l) and
addition, due to exposure of the satura
absorbing solution for a definite time (
20 min) under anaerobic conditions; incre
temperature is desirable (40−50 °C). This e
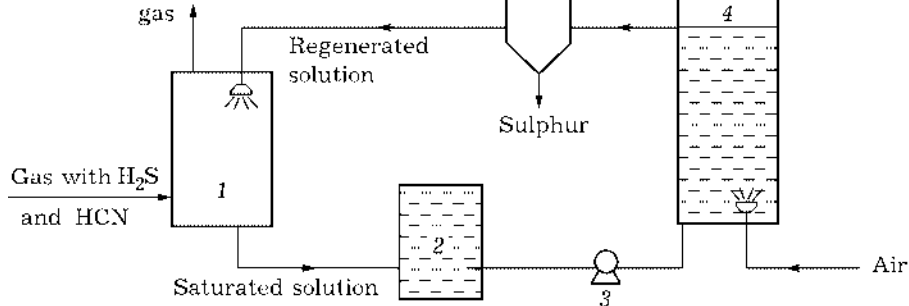sure causes more complete transformatio

Fig. 1. Scheme of simultaneous purification of the gas from hydrogen sulphide and hydrogen cyanide: 1 – absorber, 2 – reactor, 3 – circulation pump, 4 – regenerator.

A scheme of the set-up for the purification coke gas from sulphur and cyan is shown in Fig. 1. The set-up includes three major devices: absorber 1, reactor 2, and regenerator 4. The most complete transformation of the absorbed hydrogen cyanide into thiocyanate ions occurs in the reactor. Oxidation of the absorbed hydrogen sulphide into elemental sulphur proceeds in the regenerator.

Selection of optimal catalyst concentration

When choosing optimal catalyst concentration, we started from the fact that high yield of sulphur as a result of oxidation is observed at very high rate of the oxidation of HS^- ions in the diffusion region of oxidation process, when $[O_2]_{sol} \ll [O_2]_{equal}$. As a rule under these conditions high $[HS_n^-]/[O_2]_{equal}$ is observed. For this catalyst concentration, due to very high rate of HS^- oxidation into HS_n^- in solution,

the inhibiting action of SO_3^{2-} and CN^- ions substantially suppressed [21, 22].

RESULTS OF COKE GAS PURIFICATION FROM SULPHUR AND CYAN BY THE CATALYTIC METHOD

Tests were carried out with the experimental set-up of coke gas purification at the Kemerovo industrial enterprise "Khimprom", the productivity of the set-up was 200 nm³/h. The TSFK catalyst [24] was used, in which the active component is tetrasodium salt of 2,9,16,23-tetrasulphonate cobalt phthalocyanine $(CoPc(SO_3Na)_4$ or CoTSP). Coke gas under purification contained CO_2 2.2–2.5 % vol., H_2S 0.15–0.30 % vol., and HCN 1–2.5 g/m³.

As a result of uninterrupted operation of the set-up for 7 months, optimal parameters of the purification process were established. The required gas purification degree was achieved (residual H_2S <20 mg/m³). With the same

TABLE 1

Results of the purification of coke gas from H_2S and HCN with the experimental set-up at the Kemerovo IE "Khimprom" using the catalytic and arsenic-soda procedures

Purification parameter	Procedure	
	catalytic (with TSFK catalyst)	arsenic-soda
Coke gas consumption, nm³/h	100–125	90–110
Specific irrigation, m³ of liquid per m³ of gas	0.03	0.04

5 V. M. Maslennikov, Yu. A. Vyskubenko, V. Ya. St...
berg *et al.*, Porogovye ustanovki s vnutritsiklovoy ...
fikatsiyey topliva i ekologicheskiye problemy en...
tiki, in S. A. Khristianovich and T. K. Jeins (...
Nauka, Moscow, 1983.

6 L. A. Latysheva, A. P. Emelyanova, N. S. Po...
G. S. Frizler, *Koks i khimiya*, 1 (1988) 33.

7 L. F. Marakhovskiy, N. A. Sobina, V. D. Kuznetsov ...
Ibid., 6 (1989) 31.

8 Inventor's certificate, 895085 USSR, 1980.

9 Inventor's certificate, 919347 USSR, 1980.

10 N. N. Kundo, N. P. Keyer, *Kinetika i kataliz*, 11, 1 (197...

11 M. R. Hoffman, B. C. Lim, *Environ. Sci. Tech...
13, 11 (1979) 1406.

12 R. G. Luthy and S. G. Bruce, *Ibid.*, 13, 12 (1979) ...

13 E. W. Abel, J. M. Pratt, R. Whelan, *J. Chem. Soc.* ...
ton Trans. Inorg. Chem., 4 (1976) 509.

14 A. D. Simonov, N. P. Keyer, N. N. Kundo, *Kinet...
kataliz, 14, 4 (1973) 988.

15 N. N. Kundo, N. P. Keyer, *Zhurn. fiz. khimii,* 9 (1971...

16 E. W. Abel, *Chem. Commun.*, 9 (1971) 449.

17 D. M. Wagnerova, E. Schwertnerova, J. Veřek-S...
Collection of Czechoslovak Chem. Comm...
39, 8 (1974) 1980.

18 W. L. Reynolds, J. J. Kolstad, *J. Inorg. Nucl. C...*
38 (1976) 1835.

19 G. A. Faddeenkova, N. N. Kundo, *Zhurn. prikl. kh...*
71, 9 (1998) 1471.

20 G. A. Faddeenkova, N. N. Kundo, *Ibid.*, 51, 1 (1978...

21 G. A. Faddeenkova, N. N. Kundo, *Ibid.*, 52, 4 (1979...

22 G. A. Faddeenkova, N. N. Kundo, *Ibid.*, 52, 10 (1979) ...

23 A. B. P. Lever, H. B. Gray, *Accounts Chem.* ...
11 (1978) 348.

24 TU 6−09−32−41−84. Katalizator tetrasulfoftalots...
kobal'ta natriyevaya sol' (TSFK).

25 E. P. Sycheva, A. P. Denisova, G. A. Faddenkova ...
Tr. II Vsesoyuz. konf. "Kataliticheskaya ochistka g...
part 2, Novosibirsk, 1981, pp. 30−33.

method were performed. Results of the
parative tests are shown in Table 1 [25].

Thus, the method of simultaneous purifica-
... from sulphur and cyan has proved to be
... ient for purification of low-sulphur coke gas.
... minor revisions, this procedure can be used
... urify other gases obtained by thermochemi-
... processing of eastern coal; the purified gases
... then be used to obtain electric and thermal
... gy, including incineration of the purified
... s in gas turbine power installations.

Complete conversion of the absorbed H_2S
... the oxidation products is achieved at the
... e of oxidative regeneration of the absorb-
... solution. Because of this, very low H_2S
... ent can be achieved in the purified gas by
... ring H_2S absorption conditions at the stage
... bsorption (a decrease in gas/liquid con-
... ption ratio, involvement of counter-flow).
... er definite conditions, almost complete
... fication of the gas from H_2S is achieved
... dual H_2S content <1−2 mg/nm^3). The pu-
... d gas can be used as a raw material to
... in ammonia, methanol, liquid fuel.

... RENCES

... M. Zykov, *Energiya*, 11 (2001) 12.

... N. Favorskiy, E. P. Volkov, G. G. Olkhovskiy, *Ibid.*,
... 2001) 2.