Indian Journal of Chemical Technology
Vol. 25, November 2018, pp. 553-560

Dissolution of sediments and deposits in Coke-Oven-Gas purification

Buryan Petr[1] & Baran Pavel*[,2]

[1]Institute of Chemical Technology, Prague Czech Republic,
E-mail: buryanp@vscht.cz

[2]Arcelormittal Ostrava-Kunčice a.s., Czech Republic,
E-mail: Pavel.Baran@arcelormittal.com

The report focuses on the development and operational testing of an organic agent for the chemical dissolution of organic sediments in technological units of a wet ammonia system for coke-oven-gas purification – a stripping column of free and bound ammonia and a hydrogen-sulphide scrubber. The experience gained has been used in the reorganisation and subsequent long-term implementation of the desulphurisation process of raw coke-oven gas in the coking plant ArcelorMittal a.s. Ostrava.

Keywords: Coke-Oven-Gas, Deposit, Dissolution, Purification

Sediments forming in the technological equipment for coke-oven-gas purification (i.e. in a hydrogen-sulphide scrubber and an ammonia stripping column) reduce its scrubbing performance. This increases the risk of not meeting the requirement on the purity of the coke-oven gas (COG), specifically on the concentration of sulphur components in it [1,2].

The currently known methods of COG desulphurisation can be divided into the following groups [3-12]:

a) Dry desulphurisation – gas desulphurisation by solids,
b) Wet gas desulphurisation, applying either a suspension or a solution as the scrubbing solution; this group may be subdivided into
  - the methods by which hydrogen sulphide is converted into sulphur through hydrogen-sulphide oxidation;
  - the methods during which the hydrogen sulphide absorbed in the scrubbing solution is first released from the liquid and then further treated to be converted into solid sulphur or sulphuric acid;
  - combined methods by which the hydrogen sulphide from the gas binds to ammonia and is converted into ammonium sulphate, which means that desulphurisation is combined into one process with the production of ammonium sulphate.

The rationalised method of COG desulphurisation is a wet process.

The vast majority of desulphurisation studies are devoted to the actual capture of hydrogen sulphide. The goal of this work, however, was the development and application of an agent for the removal of sediments in an apparatus for the scrubbing of hydrogen sulphide and ammonia from raw COG with the aim of increasing the throughput of the technological device and the effectiveness of the scrubbing of impurities from the COG.

Description of the device cleaned

Gas cooling and hydrogen-sulphide scrubbing

The studied hydrogen-sulphide (H_2S) scrubber of the maximum hourly throughput of the COG of 80,000 m^3(101,325 kPa, 0°C) and the maximum overpressure of 20 kPa is divided into the scrubbing stage (the upper part) and the secondary cooling stage – the lower part of the absorption column.

The raw COG first enters the lower part of the H_2S scrubber, where it cools from 45–60°C (which is high above the condensation point of water vapour) to a temperature of ca 24°C. The COG is directly cooled using a mixture of ammonia water and tar. The heat gained in the secondary cooling stage is dissipated in heat exchangers by mechanically cooled water or cooling water from ventilator cooling towers.

The amount of tar in the circulating ammonia water depends on the amount of naphthalene in tar. Its amount in the mixture should not exceed 10 wt. %. The tar should dissolve the naphthalene contained in the raw COG and thus prevent the clogging of scrubbers.

Hydrogen Sulphide Scrubber

The gas, cooled in the secondary cooling stage and depleted of naphthalene, enters the central part of the H_2S scrubber, where its largest part is removed. The scrubbing media are water enriched with ammonia effluent from the first ammonia scrubber and cooled deacidified water from a deacidification column.

To prevent the exothermic heat of reaction generated in the chemisorption of impurities from having a negative impact on hydrogen-sulphide scrubbing, the absorption heat of scrubbing waters is dissipated through cooling circuits using cooling or mechanically cooled water. The temperature of the COG must be approximately 1–2 °C lower than the scrubbing-water temperature. This prevents the naphthalene from raw COG from condensing and from clogging the scrubber.

The first of the two types of scrubbing water fed to the H_2S scrubber through a heat exchanger and a cooler is deacidified water from a deacidification column. The deacidified water is first cooled in a plate heat exchanger by scrubbing water enriched with H_2S from a tank, which is thus simultaneously preheated for subsequent stripping in the deacidification column. This is followed by further cooling by cooling water in the continuing plate cooler. Before the deacidified water enters the H_2S scrubber, its temperature is regulated behind the cooler by mechanically cooled water or cooling water from cooling towers. Another medium brought to the head of the scrubber is the scrubbing water enriched with ammonia from the first ammonia scrubber.

The H_2S-enriched scrubbing water flows by gravity from the scrubber to a tank, which is to balance the amount and composition of the enriched scrubbing water, which is further regenerated.

Ammonia scrubbing

The partially desulphurised gas from the H_2S scrubber flows upwards through the first ammonia scrubber, in which it is scrubbed by countercurrent cooled detarred water fed to the centre of the scrubber by a pump from the pretreatment of phenol-ammonia water and scrubbing water enriched with ammonia from the bottom part of the second ammonia scrubber fed to the head of the first ammonia scrubber. In the scrubber, the removal of hydrogen sulphide and ammonia scrubbing continues.

The ammonium-enriched scrubbing water is fed from the bottom part of the second ammonia scrubber to the head of the first ammonia scrubber. In addition to ammonia, also further hydrogen sulphide is removed here. The scrubbing water enriched with ammonia from the bottom of the ammonia scrubber is drawn through the heat exchanger to the head of the H_2S scrubber.

The COG, freed of hydrogen sulphide and partly ammonia, leaves the head of the first ammonia scrubber and passes through the second ammonia scrubber, in which most of ammonia is removed by absorption and the gas is purified to the desired content of ammonia.

A regulated amount of the ammonia water stripped from the tank is fed by a pump to the head of the second ammonia scrubber as a scrubbing medium. Before the stripped ammonia water enters the scrubber, it is cooled in a plate cooler by mechanically cooled water or cooling water from cooling towers.

In its bottom part, the second ammonia scrubber has a scrubbing section for the final removal of H_2S and other acidic components (fine desulphurisation) from the gas. This final purification is done in countercurrent flow by diluted sodium hydroxide – approximately 2–4 %.

Experimental Section

Analysis of deposits and the development of a solvent

The laboratory tests performed in the first phase were focused on the dissolution of sediments from the H_2S scrubber and stripping columns of free and bound NH_3. Their aim was to gain knowledge making it possible to remove these undesirable substances from the current equipment without damaging it while preserving all operational parameters of individual apparatus.

The genesis of the collected samples of deposits characterising the state of the technological apparatus is shown in Table 1. An example of the clogging of a

Table 1 — Genesis of the studied samples of deposits

Sample No.	Place of collection	Note
1	Hydrogen-sulphide scrubber	A black, plastic to semisolid deposit mixed with a tarry, viscous substance
2	Bound-ammonia stripping column	A black, powdery to lumpy deposit
3	Free-ammonia stripping column	A black, powdery to lumpy deposit with discernible yellow clots

built-in structure of the H_2S scrubber with undesirable components is documented in Fig 1.

Based on the data obtained and the related technological connections, it can be stated that the organic part of the deposits is formed from the tarry substances released in coke-oven chambers during the production of coke from coal that are entrained by the exhausted raw COG depending on the prevailing thermodynamic conditions.

Because of their physicochemical properties, gases and low-molecular (i.e. also low-boiling) components are able to undergo the entire purification process. High-boiling (i.e. also high-molecular) substances 'drop out' after the raw gas is cooled and they come into contact with aqueous scrubbing media; some of them are captured in the device in the form of an undesirable deposit.

In addition to organic and inorganic compounds that are no longer active, however, the raw COG also contains a whole range of reactive carbonaceous as well as heterocyclic components, which interact with each other in the apparatus monitored while producing more or less soluble or even insoluble compounds.

The ongoing polymerisation and polycondensation reactions are i.a. catalysed here by both oxygen and various inorganic compounds from which these devices are made or which are entrained by the gas flow from coke-oven chambers (ferrous components) or from the substance being coked. A significant insoluble share of the deposits is formed by carbon, which is present in them as graphite, coke dust or soot, i.e. substances entrained from the coke-oven chambers into the exhausted raw-gas flow. Considering the high amount of iron in the deposits, some of the corrosion products captured may come from the preceding metal devices.

Fig. 1 — Detail of the built-in structure of the hydrogen-sulphide scrubber

Also gaseous substances such as hydrogen sulphide, methyl mercaptan, carbonyl sulphide, ethylene, acetylene, hydrogen cyanide, ammonia, etc. participate in the ongoing undesirable reaction. The creation of sulphur components will also be accompanied by reactions associated with vulcanizing sulphur produced through the oxidation of hydrogen sulphide.

Laboratory technology

The collected samples of deposits were first subjected to elemental analysis (Thermo Scientific Flash 1112), the assessment of ash content (850°C) and composition (ARL 9400Xp+ spectrometer) and solubility tests (a modified Soxhlet apparatus).

In the first phase, sediment solubility tests were carried out with samples weighing less than ca 1 g. After the data obtained were evaluated, the solvent disruption of the consistency of the deposits was studied with the application of a larger volume of solvents with charges exceeding 50 g.

Elemental analysis

Building on the initial findings from the use of organic solvents and their mixtures in the disruption of the compactness of the sediment sample from the hydrogen-sulphide scrubber, elemental analysis seemed desirable. It was important mainly to determine the content of combustible sulphur, which is very likely to comprise a significant part of high-molecular-weight polymer deposits in the form of polymer bridges of vulcanising character.

Ash-content assessment

Although the aim of the laboratory study was to develop an agent that would be able to remove the deposit from the hydrogen-sulphide scrubber, i.e. mainly its organic phase, it was necessary to ensure both the absolute organic content in the deposit and its distribution after the application of the solvent developed. These indicators were determined i.a. through ash-content assessment.

It should be emphasised that this parameter does not reflect precisely the content of inorganic compounds, because many of those present in the sediments observed are subject to thermal destruction during ash assessment. These include mainly inorganic ammonium salts, carbonates, cyanides, sulphides, disulphides, etc.).

Ash composition

In order to determine the origin of the inorganic share of the sediments, the composition of ash was assessed for a selected number of samples (ARL 9400Xp+ spectrometer) with the aim of ascertaining whether these were corrosion products of the metal parts of apparatus or ash matter from coal or abraded particles from coke-oven chambers. The actual results of these analyses are in the text below for each sample including the estimated origin.

Development of Solvent

Based on long-term research activities related to studies of the composition of sediments from tars of diverse provenance, from crude-oil and natural-gas extraction, coal-gas and crude-oil distribution etc., the laboratory gradually tested various standard organic compounds, then mixtures of paraffinic, olefinic and aromatic hydrocarbons and later also heterocyclic compounds. The subsequent part of the laboratory study focused on the additions of 0.1–5 wt. % of surfactants increasing the solubility of the organic share of the sediments and the dispersibility of inorganic parts of the sediments in a solvent. In the final phase, organic corrosion inhibitors were added to the developed mixture of organic compounds.

The aim of the laboratory study was not 100% dissolution of sediments. A positive result was also a mere disruption of the compactness of the sediments forming a solid deposit on the structures inside the scrubbers, making it possible to leach a deposit from the apparatus by a circulating substance.

The selection of the solvent focused mainly on industrially available, high-tonnage-produced substances, because the aim was yearly operational application.

What was mainly taken into account in the development of the new preparation were the economic-technological demands of its application, adequate economic availability, the possibility of easily preparing the composition under operational conditions, the safe storage life of the individual ingredients or their mixtures (including winter months), the exclusion of undesirable corrosive impact of these substances on steel structures, final control elements and measuring equipment, easy application under real operating conditions of the coking plant (including winter months, rain, etc.). Important aspects were the liquidation of the applied products after the treatment and the environmental impact of the process developed.

The amount that could be dissolved in the plant from the hydrogen-sulphide scrubber was assessed using an extraction apparatus fitted with a reflux condenser. A sample of the sediment was weighed into a paper thimble hung such that the solvent level could not leach the undissolved part of the deposit from the thimble. The heating temperature of the solvent was set by an electric heating mantle never to exceed ca 150°C, which respected the future thermodynamic conditions of a technological plant. The effect of the solvent was evaluated mainly gravimetrically.

The most promising was a mixture of organic compounds comparable to a fraction of coke-oven tar with a with a boiling point below 215 °C with additions of ca 0.1–3 wt. % of surfactants (amine organic acid) and ca 0.01–1 wt. % of corrosion inhibitors (organic alcohol).

Results and Discussion

Hydrogen-sulphide scrubber deposit

Since the character of the collected scrubber sediment sample was, because of its consistency, impossible to homogenise, elemental analysis was not performed in this case. It was carried out only for the insoluble residue of the deposit. On average, it contained 3.17 wt. % of noncombustible share.

In general, it can be stated that the developed solvent dissolved up to 95 wt. % of the deposit. When the most suitable surfactant was used, it was even 97 wt. %. It should be emphasised here that the addition of a surfactant made it possible to dissolve all sulphur components from the deposit – Table 2.

Another significant finding is the fact that the weight of the insoluble residue in the paper thimble used was always lower than the weight of the ash in the raw deposit. This means that the numerous inorganic elements and carbonaceous components were so small that they passed through the pores of the thimble walls into the filtrate.

Table 2 — Elemental analysis of the insoluble residue – % by weight

Element / Parametr	N	C	H	S*)	Sum
Content	1.51	58.78	1.80	0.37	58.92
Solvent + surfactant	1.33	67.50	2.05	<	69.55

*) combustible, < below the detection limit of the method used

Ash composition

The composition of the ash from the insoluble part of the deposit from the hydrogen sulphide scrubber listed in Table 3 implies that the dominant elements are iron, sulphur, silicon and aluminium, followed by calcium, zinc, lead and titanium.

The calcium comes from the water used. The origin of the iron, aluminium, zinc, lead and titanium rather corresponds to the corrosive products of construction steel. The presence of the silicon is likely to have its origin in the pollution associated with maintenance. The sulphur probably originates from COG. Based on the ash composition, however, one cannot exclude the possibility of the priming of the solid matter from coke-oven chambers by the COG.

Deposit from the stripping colum of the Bound ammonia

The average values of the elemental analysis of the deposit and the assessed ash content are summarised in Table 4.

The solvent developed mainly for the hydrogen-sulphide scrubber dissolved 45 wt. % of this deposit. It must be emphasised here, however, that the deposit contained around 28 wt. % of ash on average, which means that approximately a half of the insoluble residue is always formed by inorganic incombustible matter. In general, the organic solvent thus dissolves more than a half of the organic matter of the sediment.

The data on the composition of the ash from the deposit of the bound-ammonia stripping column listed in Table 3 indicate that the dominant element in the ash is iron. It reaches ca 92 wt. %. The content of the next three elements is about 1 wt. %. It is thus evident that the inorganic share of the deposit is very likely to be a corrosive product of the construction material(s).

Deposit from the free-ammonia stripping column

The average values of the elemental analysis of this deposit and yellow admixtures mechanically separated from it are summarised in Table 5.

The content of combustible sulphur in Sample 3 is approximately twice as high as that in Sample 2. This is connected with separately analysed 'yellow' particles, which were practically sulphur elements. The average content of the incombustible share of the sediment was 22.25 wt. %. This is less than in the case of Deposit 2.

The solvent developed mainly for the hydrogen-sulphide scrubber at temperatures reaching up to ca 150°C dissolved 35 wt. % of this deposit, which means that ca 65 wt. % was an insoluble residue. In the application of a solvent mixture with the addition of a surfactant, the amount of the dissolved part reached ca 40 wt. %. With the addition of 1 % of a corrosion inhibitor, the solubility reached ca 65 wt. %. Yet it needs to be emphasised here as well that the deposit contains around 22 wt. % of ash on average,

Table 4 — Elemental analysis and ash content of Sample 2 – % by weight

Element / parameter	N	C	H	S*)	ash
Content	15.96	46.02	3.08	2.51	28.58

*)…combustible

Table 3 — Ash composition – % by weight

Element	Sample No.1*)	Sample No. 2	Sample No. 3	Element	Sample No.1*)	Sample No. 2	Sample No. 3
Al	5.41	0.86	0.55	Mn	0.14	0.28	0.22
Ba	0.09	0.09		Na	0.18	0.90	2.35
Bi		0.02		Ni	0.18	0.04	0.03
Ca	1.67	0.53	0.36	S	7.56	0.75	1.31
Cl	0.78			Si	6.83	1.04	0.71
Co		0.13		Ti	0.59	0.07	0.05
Cr	0.04	0.05	0.04	Fe	9.55	91.70	90.90
Cu	0.01	0.06	0.03	Pb	1.42	0.09	
Hg	0.14			Sn	0.09		
K	0.64	0.25	0.33	Zn	1.44	1.40	1.23
Mg	0.17	1.69	1.79	P	0.05	0.03	0.02

*) the residue from the dissolution of the deposit

Table 5 — Elemental analysis and the content of ash in Sample 3 and separated admixtures – % by weight

Element / parameter	N	C	H	S*)	ash
Sample 3	14.87	51.68	3.28	4.13	22.25
Yellow particles	0.10	0.20	0.02	96.49	–

*)…combustible

which means that approximately one-third to one-half of the insoluble residue is formed by inorganic incombustible matter.

The data on the composition of the ash from the deposit from the free-ammonia stripping column indicate that the dominant element in the ash is iron. Its content reaches ca 91 wt. %. The content of the next three elements (sodium, magnesium and sulphur) is 1–2 wt. %. It is thus evident that the inorganic share of also this deposit is very likely to be a corrosive product of the construction materials.

Testing of undesirable properties of solvent

Along with the samples of the deposits, typical samples of sealants used in various parts of the operational equipment of a coke-oven plant were studied under laboratory conditions in order to make sure that the developed agent does not have undesirable effects on them.

For this purpose, the sealants including PALL rings from the inside of the NH_3 stripping columns were immersed in the developed agent for 5 months. After they were removed, they exhibited no apparent side effects of the agent.

Course of experiment

The actual application of the newly developed solvent was begun by adding ca 40 kg of a surfactant to 8 m^3 of a solvent. After heating to ca 150°C, the content of the tank was pumped into the upper part of the scrubber, from where the liquid flowed down through a 10-meter (five-layer) rib mesh structure, specifically through collecting and separating levels with height-adjustable overflows, to the bottom part of the aggregate. This was followed by a 30 hr washing of the scrubber. The effect of the solvent is evident in Fig. 2.

Fig. 2 — The upper part of the H_2S scrubber after the application

It was not necessary to use the defoamer prepared, because during the cleaning of the scrubber the problem with the formation of foam did not occur. The same applies to the corrosion inhibitor.

Evaluation of operational experiment

Before the operational testing of the agent developed and after its application, the pressure difference and temperature of the COG before and behind the H_2S scrubber were regularly monitored for several days. The measurement results summarising the change in the difference pressure before and after the cleaning characterising the thermodynamic resistance to the flow of the COG through the scrubber are illustrated for better clarity in the form of a graph in Fig. 3 , showing the regression curve well covering the pressure difference recorded. It is obvious from the data shown that the demonstrated average pressure change after the scrubber was cleaned by the agent developed was 530 Pa.

The results of the COG temperature measurement are recorded in Figure 4. As arises from the evaluation of these data, the demonstrated average temperature change of the COG after the scrubber was cleaned by the agent developed was 3.7 °C.

Laboratory analysis of the solvent used

After the agent heated to ca 70 °C was sprayed on the top level of the structure built in the H_2S scrubber, i.e. after it first passed through the scrubber and was

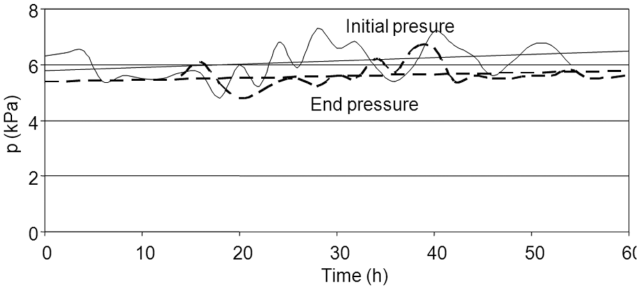

Fig. 3 — Comparison of difference pressures

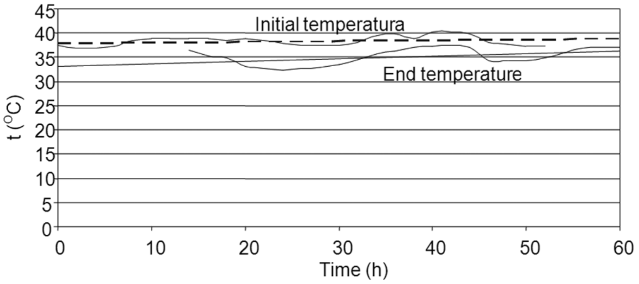

Fig. 4 — Comparison of temperatures

circulated for 24 hr by the pump of the scrubber, samples of the applied agent were collected. Their basic analysis characterising the effect of the agent on the sediments in the scrubber can be summarised as follows.

Both samples collected formed dark-brown liquid without apparent significant water parts. After they were poured into glass cylinders of a diameter of ca 6 cm, an attempt was made to screen the samples by an electric table lamp and thus determine the concentration of various inclusions, villi, etc. The samples, however, were so saturated by the dissolved sediments that they could not be screened by a 100W light bulb. Fourteen days later, the two samples placed in measuring cylinders were carefully subjectively divided into the upper, 'less' dense, and lower, 'dense-to-villous', parts. In the sample collected immediately after the spraying, the 'dense' part, separated by sedimentation, represented ca 30 vol. %. In the sample collected after 24-hour circulation, the 'dense' part, separated by sedimentation, represented ca 43 vol. %.

It is hence evident from this finding that sediments were substantially removed already after the agent first passed through the scrubber, when it merely flowed down the scrubber filling. Likewise the 43 vol. % share of the 'dense' part in the solvent sample collected after its 24 hr application clearly documents its effectiveness in removing the deposit.

For the assessment of the content of the dissolved sediments in the agent used, distillation curves were determined in both samples as well. The values obtained, complemented by the content of the water separated by distillation and the subsequent simple sedimentation, are listed in Table 6.

From Table 6, one can derive further information on the cleaning progress and efficiency. If one proceeds from the assumption that the agent used should mainly consist of substances with a boiling point below 210°C, then the substances with a boiling point above 210°C formed 18 vol. % already after the agent first passed through the scrubber and the proportion of substances boiling above 210°C further increased in the sample after a 24 hr application to 28 vol. %, which means that it formed more than one-quarter of the absolute volume distilled. If the same is expressed for an unhydrous distillate, the substances boiling above 210°C form ca 21 vol. % after the agent first passes through the scrubber. After a one-day application, it is already ca 34 vol. %., which is ca one-third of the sample taken.

Another important finding is information on the non-distilled share. In the sample before recirculation, the absolute content of non-distilled components under laboratory conditions was 14 vol. %., in the sample after the 24 hr recirculation 20 vol. %. When applied to an unhydrous distillate, these values are ca 16 % and 25 %.

Insoluble Matter

A classic procedure applied when studying the properties of COG is to determine the content of the substances insoluble in toluene. Through the application of this method for the two samples collected, it was discovered that the content of the substances insoluble in toluene in the sample before recirculation was 0.25 wt. % and in the sample after 24-hour recirculation it was 0.27 wt. %.

Based on the values above, it can be assumed, in connection with the obvious appearance of the built-in

Table 6 — Comparison of the distillation curves

Volume (mL)	Temperature (°C)		Water volume in the distillate (mL)	
	before recirculation	after recirculation	before recirculation	after recirculation
Beginning	93	93		
5	95	96	2	2
10	97	96	5	5
20	108	96	10	13
28	111	100	14	15
30	172	110		17
35	174	172		
40	176	179		
50	178	183		
60	182	193		
70	187	205		
80	200	230		
85	225			

structure after the cleaning of the scrubber, that the agent used removed the sediments from the scrubber in a form that can be well applicable outside the device concerned.

The separated substances insoluble in toluene were repeatedly burnt at 850°C in a muffle furnace with the aim to determine the content of inorganic substances in the agent used. This method also revealed a trace amount of ash in the samples studied.

No apparent problems were recorded when the polluted agent was transported outside the technological part of COG purification.

Conclusion

The developed mixture of solvents very efficiently dissolved crusts from NH_3 stripping columns and a H_2S scrubber in the system of COG purification. In the case of the H_2S scrubber, the solvent functionality is verified by an operational experiment as well.

Sediment dissolution saves costs on the mechanical cleaning of the scrubber, which has been done twice a year. This is, however, only the profit arising from a comparison with the mechanical cleaning of the upper chutes and the bottom, when the rib mesh structures remained clogged. For them to be cleaned, it was necessary to put the unit out of operation, during which the built-in rib mesh structures had to be disassembled and cleaned outside the scrubber. Improving cleaning performance will reduce the content of impurities in the COG, which will be positively reflected in the distribution of the COG as well as in the operation of numerous devices of final energy consumers. Less maintenance and cleaning work on technological equipment will improve the safety and hygienic working conditions.

References

1 Mohit N, Randhir S, Naveen K & Sushan U, *Int J Sci Res Rev,* 2 (2013) 13.

2 Liao H , Li B & Zhang B, *Fuel*, 77 (1998) 1643.

3 Baker W J W, Kapteijn F & Moulijn J A, *Chem Eng J,* 96 (2003) 223.

4 Qi G, Liu Z & Jiao W, , *China Petrol Proc & Petrochem Techn,* 13 (2011) 29.

5 Massey M J & Dunlap R W, *J Air Polutl Contl Assoc,* 25 (1975) 1019.

6 Sowa F, Otten B, Kamp J & Proface E, Advanced technologies for desulphurization of coke oven gas, COG *Desulfurization*, ICC 2009, Ranch, India.

7 Platonov O I, *Coke Chem, 50* (2007) 226.

8 Berg T & Barry J, By-Product Practice, Ironmak. Conf. Proc. 61 (2002) 371.

9 Kohl A. & Nielsen R.: Gas purification, Houston, Texas: Gulf Publishing, 1997.

10 Stemphen R, Tseslyer R, Toma S & Zaodel R, *Coke Chem,* 44 (2001) 22.

11 Ukhmylova G S, *Coke Chem,* 43 (2000) 30.

12 Rauf R, Chushan L & Soujiang Z, *Fuel,* 113 (2013) 287.