

<https://doi.org/10.3176/oil.1997.2.04>

POSSIBILITIES OF DEEPER DESULFURIZATION OF FLUE GASES BY OIL SHALE ASH COMPONENTS IN DIFFERENT BURNING TECHNOLOGIES

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Generalization and analysis of experimental data show the increasing of the SO_2 content in flue gases with the growth of steam load for all the types of oil shale boilers. The SO_2 concentration can be presented in some approximation as a function of the boiler furnace heat liberation q_v in the following form: $SO_2 = 0.0165 q_v$. On the basis of created mathematical models a program complex has been developed allowing to calculate the SO_2 removal efficiency by oil shale components and additional sorbent based on CaO. Test calculations indicate that the role of different factors on the SO_2 removal process (such as gas temperature, particles concentration, size distribution and structure, interaction time, place of installation of additional sorbent nozzles, etc.) may be evaluated. In the 42-74 % range the calculated values of the SO_2 removal efficiency agree satisfactorily with experimentally determined ones.

Introduction

The problems of power engineering development of regions and ecological problems are connected closely. At the present time a considerable reduction of power consumption and output takes place in Estonian economy due to the industrial depression. It has led to reducing harmful outbursts at Estonian power plants and, as a result, decreased

temporarily acuteness of ecological problems. However, ecological problems will arise again in consequence of expected economical stabilization and the following growth of power consumption unless new effective combustion technologies are developed.

The problem of desulfurization of flue gases when combusting Estonian oil shale is the most complicated question of nowadays. The searching for the solution of this problem in common with foreign companies has been carried out for several years. Some methods of desulfurization of flue gases have been practically tested but their application is too difficult and these methods do not take into account all peculiarities of mineral matter of the fuel quite well. Under these circumstances it is necessary and very actual to examine the whole spectrum of solutions concerning the problem of oil shale combustion.

Analysis of the Results of Experimental Research

Different institutions in co-operation with the State Enterprise "Eesti Energia" and power plants have carried out the research of sulfur removal from flue gases by oil shale ash in order to get representative data about the real content of SO_2 in flue gases. The data measured for TP-17, TP-67 and TP-101 boilers on their operation are the most interesting, representative and complete now [1, 2]. Therefore they may be taken for the basis in the analysis of the role of different factors in SO_2 -removal process from flue gases.

Different methods and devices were used when carrying out the research. In the work [1], an automatic optical-acoustic gas analyser UNOR-6N (Meichan, FRG), Evdiometer-II, and ion exchange chromatography were simultaneously used for the measurements. In the work [2], the SO_2 content in the flue gases was measured with the help of different automatic analysing systems such as SO_x -analysers "Teco" and "Thermoelectric 43H", NO_x -CLD ELhT analyser and others.

Comparable results were obtained using different methods and types of analysers. The method of measuring the SO_2 content in flue gases by automatic optical-acoustic gas analyser UNOR-6N is the standard method used in Russia. Therefore the results obtained with the help of this method and ion exchange chromatography were used when analysing the data [1].

The results of the SO_2 content measurements in flue gases depending on the boiler load are presented in Fig. 1. Examination of these curves enables to conclude the following:

1. Absolute values of the SO_2 content in flue gases considerably depend on the measurement method. The SO_2 concentration values presented in [2] exceed by 60-70 % the values measured for the corresponding types of boilers during the work [1].

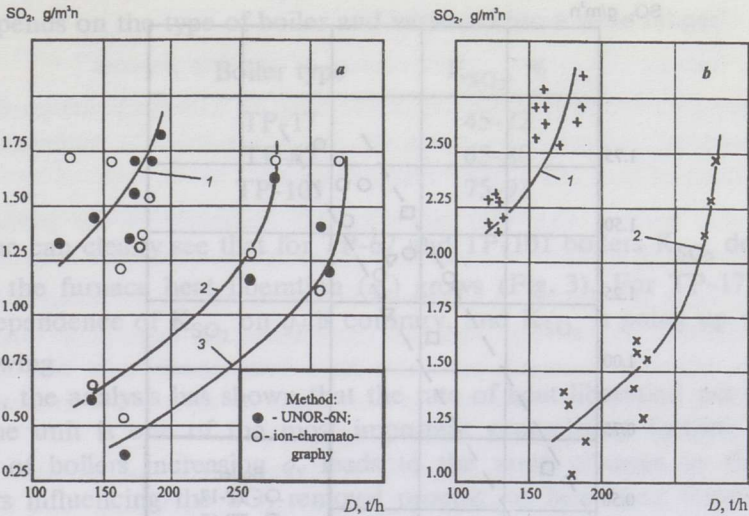


Fig. 1. The SO_2 content in flue gases of shale boilers depending on the boiler load (D): a - from ref. [1]; b - from ref. [2]; 1 - TP-17 boiler; 2 - TP-67 boiler; 3 - TP-101 boiler

- The curves shown in Fig. 1 have the same qualitative character independently on the measurement method. The SO_2 content in flue gases increases with the growth of boiler steam load for all types of boilers. At loads close to the nominal loads of boilers a considerable increase in SO_2 discharge level takes place.
- The SO_2 concentration in stack gases and SO_2 -removal efficiency depend on the type of the boiler: TP-17 boilers have the highest SO_2 discharge level, and TP-101 boilers have the lowest one.

Ratios of the maximum measured SO_2 concentration to the minimum one for the boilers are the following: TP-17 - 1.4; TP-67 - 2.83; TP-101 - 4.85. TP-17 boilers are the most unfavourable concerning the SO_2 discharge level. At the average operation load the SO_2 concentration in final gases for TP-17 boiler is 15 % higher than that for TP-67 boiler and 45 % higher than that for TP-101 boiler.

- As seen from Fig. 2, the SO_2 concentration in final gases depends on the rate of heat liberation per furnace volume unit and may be described (within the whole boiler operation load range) by the following linear approximation:

$$\text{SO}_2 = 0.0165 q_v \quad (1)$$

where SO_2 - the SO_2 concentration value, g/m^3

($p = 0.1 \text{ MPa}$; $t = 0 \text{ }^\circ\text{C}$; on dry flue gas basis)

q_v - the furnace heat liberation, kW/m^3

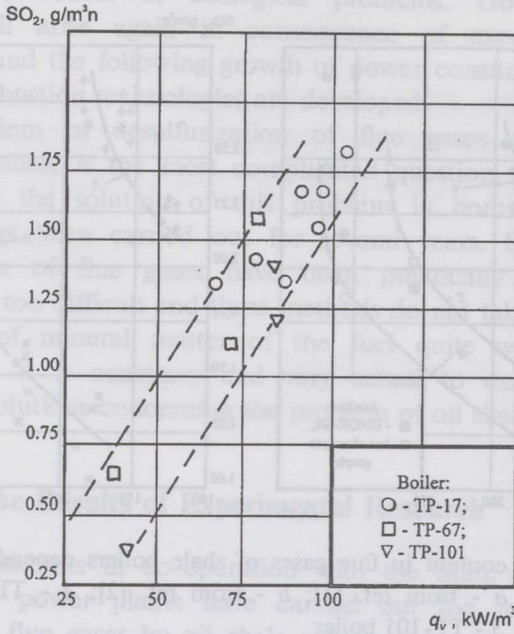
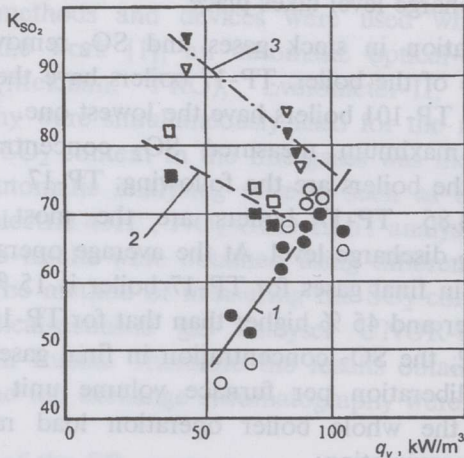


Fig. 2. The SO₂ content in flue gases of shale boilers depending on the furnace heat liberation (q_v); from ref. [1]



- 1 - TP-17 boiler; ● - UNOR-6N; ○ - ionchromatography
- 2 - TP-67 boiler; ■ - UNOR-6N; □ - ionchromatography
- 3 - TP-101 boiler; ▼ - UNOR-6N; ▽ - ionchromatography

Fig. 3. SO₂-removal efficiency by oil shale ash depending on the furnace heat liberation (q_v); from ref. [1]

5. The efficiency of SO_2 -removal by oil shale components (K_{SO_2}) depends on the type of boiler and varies within a wide range:

| Boiler type | K_{SO_2} , % |
|-------------|-----------------------|
| TP-17 | 45-72 |
| TP-67 | 65-80 |
| TP-101 | 75-93 |

One can clearly see that for TP-67 and TP-101 boilers K_{SO_2} decreases when the furnace heat liberation (q_v) grows (Fig. 3). For TP-17 boiler, the dependence of K_{SO_2} on q_v is contrary, and K_{SO_2} is going up when q_v is growing.

So, the analysis has shown that the rate of heat liberation per furnace volume unit is one of the most important generalizing factors. For all types of boilers increasing q_v leads to the same changes in the main factors influencing the SO_2 -removal process: to increasing temperatures in the furnace and increasing gas flow velocities which is equivalent to reducing the residence time of absorbing particles at the maximum reaction rate zone of the furnace. This fact explains higher SO_2 concentrations in the final gases and decreasing K_{SO_2} for TP-67 and TP-101 boilers with a direct-flow.

The opposite character of the same data for TP-17 boilers is evidently connected with special properties of the burning process aerodynamics. The burners placed in the corners of the furnace chamber of a TP-17 boiler evoke unforeseen changes in aerodynamics when the boiler load is changed during operation. It tells on the temperature regime in the furnace and on the residence time of SO_2 -absorbing ash components at the maximum reaction rate zone. These specific properties of the TP-17 boiler operation are evidently the reason for data dispersion for the boilers of this type and for less influence of the boiler loading on the SO_2 -capture efficiency.

Therefore, it is clear that a profound analysis of the SO_2 -capture process is needed and it is possible using scientifically-grounded polyfactorial mathematical models as burning and chemical processes have an extremely complicated nature.

Mathematical Model

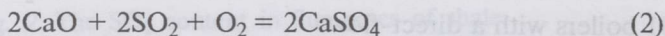
Experimental and physical modelling of the SO_2 -removal process in the furnace of a steam boiler is too expensive and difficult. In this case mathematical modelling is a more expedient method for investigation of the motion, heat exchange and interaction of oil shale components (or additional sorbents) in burning processes.

As the existent experience shows, the main factors influencing SO₂-removal efficiency are the following:

- Boiler furnace design and aerodynamics of burning process
- Burning process conditions (residence time of ash (sorbent) particles in zones of different temperature; sorbent particle concentration; conditions of heat and mass exchange, etc.)
- Chemical sorbent type and its properties (diameter of the particles, pore structure, diffusion and kinetic characteristics, etc.)

In our work the model of CaO and SO₂ interaction was taken for the basis. Attempts to develop and use mathematical models to express analogous physical-chemical processes have been made time and again [3, 4]. The Random Pore model has been used to express the interaction between solid sorbent particles (CaO) and SO₂ [4].

The sorbent particle is considered to be spherical and porous. The pore structure represents a set of randomly overlapping and size-distributed pores describable by the normal (Gaussian) pore-size distribution equation. The reaction between CaO and SO₂ (2) is considered to take place mainly on the internal pore surface.



When developing the model of chemical interaction, the following assumptions were made:

- The reaction order (n) equals 1.0 with respect to SO₂ and it equals 0 with respect to CaO and O₂
- Reaction (2) occurs on the reaction surface only
- The solid reaction product occupies a larger volume than the reactant consumed (CaO). The model foresees the possibility of reaction cessation because of the pore closure
- The reaction surface moves in the normal direction to the initial pore surface (Fig. 4)
- Co-ordinates of the reaction surface and the pore surface depend on the volume of CaO conversion into CaSO₄ (α) at the moment of their determination
- As reaction (2) proceeds, the layer of the product (CaSO₄) offers a diffusion resistance to the flow of SO₂.

With the above-mentioned assumptions, the Random Pore model [3] gives the following equation for CaO conversion (α):

$$\frac{d\alpha}{d\tau} = \frac{C^*(1-\alpha)[1-\psi \lg(1-\alpha)]^{0.5}}{1+0.5\beta(1-\alpha)Y[1-\psi \lg(1-\alpha)]^{0.5}} \quad (3)$$

$$\text{where } Y = \int_{(1-Z)\alpha}^{\alpha} \frac{d\alpha'}{(1-\alpha')^2 [1 - \psi \lg(1 - \alpha')]}$$

The concentration of SO_2 on the reaction surface was defined under the conditions of mass transfer processes. The four main resistances to mass transfer were taken into consideration (Fig. 4):

- Diffusion resistance of particle boundary layer (R_1)
- Diffusion resistance inside the pores of the particle (R_2)
- Diffusion resistance of product layer (R_3)
- Kinetic resistance on the reaction surface (R_4)

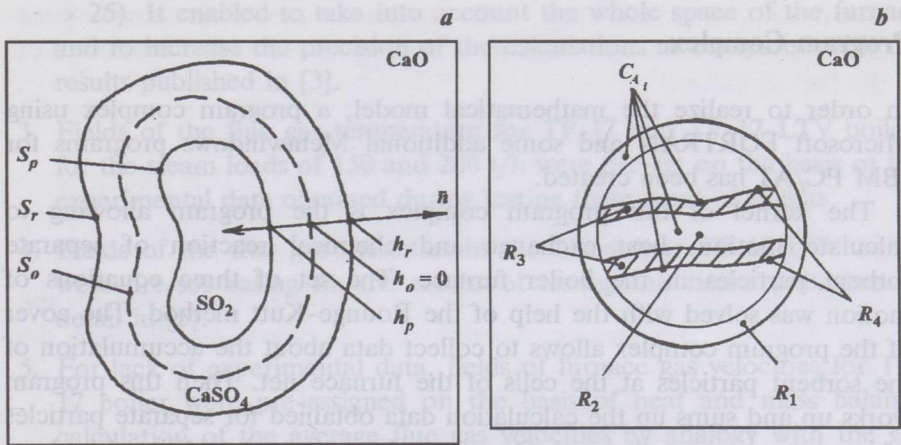


Fig. 4. Diagram of conversion inside a pore of a particle (a) and the chart of diffusion resistances to the flow of SO_2 (b): S_o , h_o , S_r , h_r , h_p - initial pore surface and its co-ordinate; surface of the reaction and its co-ordinate, respectively; n - normal to the reaction surface; R_1 , R_2 , R_3 - diffusion resistances: 1 - outside, 2 - inside, 3 - in the product blanket, R_4 - kinetic resistance of the reaction surface; C_{A_i} - the SO_2 concentration on the reaction surface

When calculating the SO_2 concentration on the reaction surface, the following average kinetic parameters were used:

- Activation energy $E = 56.4 \times 10^3$ (kJ/kmol)
- Pre-exponential factor $k_0 = 1.906 \times 10^{-2}$ (s⁻¹)

As the reaction (2) proceeds, the particle mass changes depending on the amount of conversion (α) of CaO into CaSO_4 and it can be described by the equation:

$$m_p = [\rho_{\text{CaO}}(1 - \alpha) + \alpha \rho_{\text{CaSO}_4}] \frac{\pi \delta^3}{6} \quad (4)$$

Three-dimensional motion of sorbent particles in the furnace space was described by a set of three equations – the Meshchersky Equation written in projections on the axes of a right-angled co-ordinates system [3]. Drag force, inertial force, and particle weight were taken into account as the main forces influencing the particle motion.

Heat exchange between the particle and gas flow is describable by the Equation (5) of convection and radiant heat exchange with environment.

$$\frac{dT_p}{dt} = \frac{6Nu\lambda_g}{c_p\delta^2\rho_p}(T_g - T_p) + \frac{6\varepsilon\sigma_0}{c_p\delta\rho_p}(T_g^4 - T_p^4) \quad (5)$$

Program Complex

In order to realize the mathematical model, a program complex using Microsoft FORTRAN and some additional Metawindows programs for IBM PC/AT has been created.

The kernel of this program complex is the program allowing to calculate motion, heat exchange and chemical reaction of separate sorbent particles in the boiler furnace. The set of three equations of motion was solved with the help of the Runge-Kutt method. The cover of the program complex allows to collect data about the accumulation of the sorbent particles at the cells of the furnace net. Then this program works up and sums up the calculation data obtained for separate particles taking into account the quantity of the burners and additional sorbent nozzles. As a result, it calculates the total amount of CaO converted into CaSO₄ and, consequently, the total amount of SO₂-removal efficiency

The program complex allows to simulate different variants of the sorbent feeding into the furnace at various regimes of the boiler operation.

Initial Data for Calculations

Initial data for calculating the SO₂-binding process were the following:

- Fields of temperatures and velocities of the flue gas
- The installation co-ordinates of the burners
- The installation co-ordinates of additional sorbent nozzles
- Initial velocities of discharge of the fuel and the sorbent particles
- Rate of discharge, fraction and chemical composition of the sorbent and the fuel
- SO₂ concentration in the boiler furnace

The main additions, assumptions and simplifications made when compiling initial data for the calculation of the furnace processes in TP-17 and TP-17-LTV boilers were the following:

1. SO_2 concentration was taken to be constant and equal $1.6 \times 10^{-5} \text{ kmol/m}^3$ all over the inner space of the furnace. This value fits average SO_2 concentration level in the furnaces of TP-17 power steam boilers [4]. In the real conditions SO_2 concentration fields change due to the processes of SO_2 generation and capture. However, at this stage of the program complex developing it was impossible to carry out the calculation of SO_2 generation processes.
2. In this work, the quantity of cells was increased up to 4200 ($8 \times 21 \times 25$). It enabled to take into account the whole space of the furnace and to increase the precision of the calculations as compared with the results published in [3].
3. Fields of the flue gas temperature for TP-17 and TP-17-LTV boilers for the steam loads of 150 and 200 t/h were pre-set on the basis of the experimental data obtained during testing these types of boilers.
4. Fields of the flue gas velocities in the furnace of TP-17-LTV boiler were pre-set basing on the results of testing this boiler published in detail in [5].
5. For lack of experimental data, fields of furnace gas velocities for TP-17 boiler were pre-assigned on the basis of heat and mass balance calculation of the average flue gas velocities by analogy with the gas velocity fields which were partly presented in [5].
6. The fields of the flue gas velocities were pre-set without taking into account the turbulent pulsing of the gas flow. Consequently, the gradients of calculated particle velocities are low and the model of their motion does not account the possibilities of hard braking or acceleration of the sorbent particles.
7. The particles of pure CaO were taken as a sorbent in the calculations instead of CaCO_3 which is supplied into the boiler furnace in real operation conditions. As it was shown in our earlier work [3], the reaction of CaCO_3 conversion into CaO can be neglected as a first approximation.
8. When calculating CaO and SO_2 interaction, (1) it was kept in mind that the process of CaSO_4 decomposition predominates at temperatures higher than 1200°C . At this stage of the work the CaSO_4 decomposition reaction was not taken into account. The reaction (1) was just thought to stop as a particle temperature reaches 1200°C .

The calculation of conversion (α) might be resumed if only the particle temperature drops.

9. Consumption of the sorbent supplied through the burners was taken to be equal to the pure CaO consumption that can be derived from initial calcite (CaCO_3) entering the furnace with fuel. The same consumption (1.115 kg/s) of the sorbent (CaO) is expected to be supplied through every burner. So the total CaO-consumption through all four burners is equal to 4.47 kg/s ($4 \times 1.115 = 4.47$ kg/s). The consumption of the sorbent (CaO) entering the furnace through the additional nozzles; their installation co-ordinates and optimal initial velocities of sorbent particles were determined from calculation.
10. Fractional composition of CaO particles supplied to the furnace through the burners was taken to be equal to fractional composition of the fuel as follows:

$$\text{TP-17-LTV boiler: } R_{90} = 78 \%$$

$$R_{1000} = 13 \%$$

$$\text{TP-17 and TP-67 boilers: } R_{90} = 46 \%$$

$$R_{200} = 18 \%$$

Several variants of particle size distribution which were tested for the sorbent entering the furnace through the additional nozzles are the following:

1. $R_{56} = 50 \%$; $R_{100} = 10 \%$
2. $R_{56} = 65 \%$; $R_{100} = 15 \%$
3. $R_{56} = 78 \%$; $R_{100} = 36 \%$
4. $R_{56} = 81 \%$; $R_{100} = 10 \%$

Calculation of Desulfurization Process Occurring in the Furnaces of TP-17 Boilers

Calculations of the binding process of sulfur oxides were subdivided into three following stages:

Stage 1

Calculation of the reaction of single CaO particles in the furnaces of TP-17-LTV and TP-17 boilers at 100 % of their nominal load.

The particles were injected into the furnace through the burners and the additional nozzles for the sorbent.

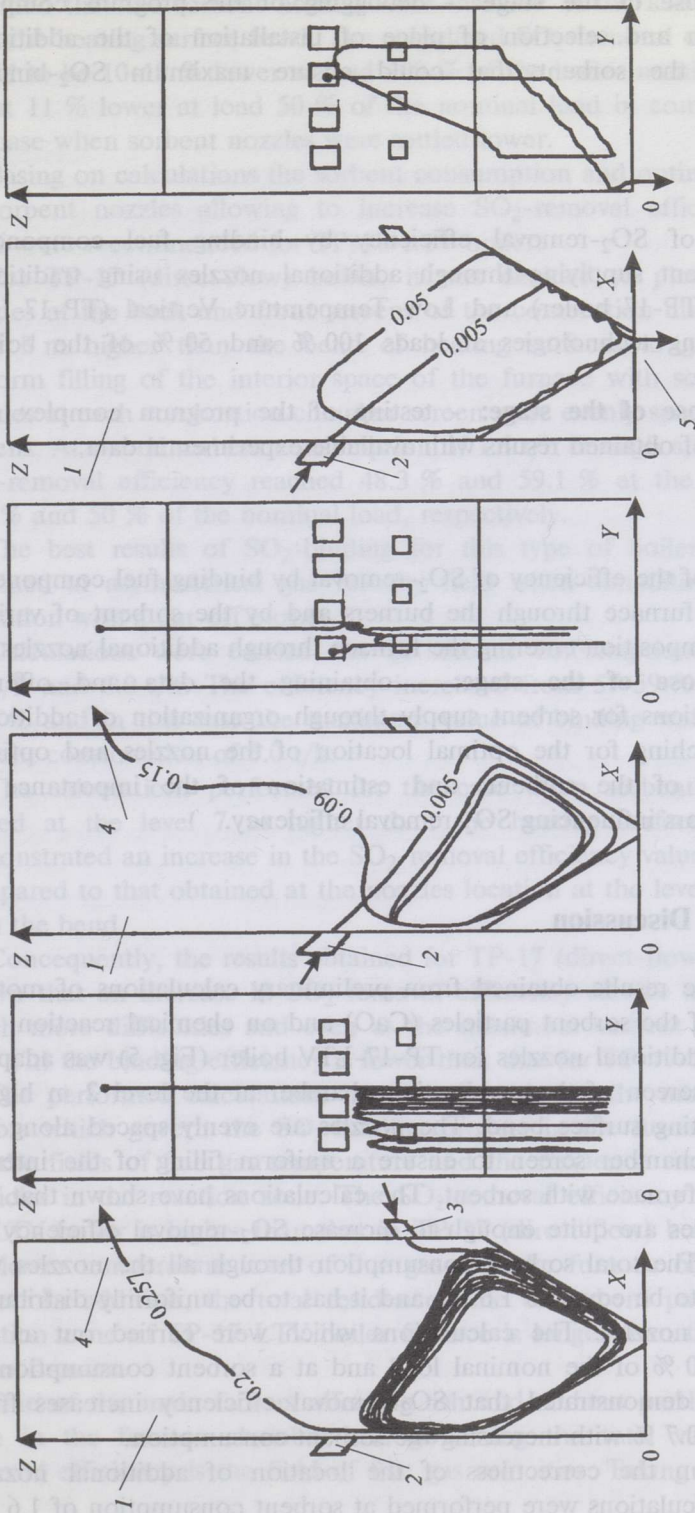


Fig. 5. The calculation results of motion trajectories of the pure CaO sorbent particles (δ) and CaO conversion (α) calculated for TP-17-LTV boiler: 1 - furnace, 2 - burner, 3 - nozzle, 4 - furnace exit, 5 - furnace slag

The purpose of the stage: - debugging of the program complex, determination and selection of place of installation of the additional nozzles for the sorbent that could ensure maximum SO₂-binding efficiency.

Stage 2

Calculation of SO₂-removal efficiency by binding fuel components without sorbent supplying through additional nozzles using traditional direct-flow (TP-17 boiler) and Low Temperature Vertical (TP-17-LTV boiler) burning technologies at loads 100 % and 50 % of the boilers nominal load.

The purpose of the stage: - testing of the program complex and comparison of obtained results with available experimental data.

Stage 3

Calculation of the efficiency of SO₂-removal by binding fuel components entering the furnace through the burners and by the sorbent of various fractional composition entering the furnace through additional nozzles.

The purpose of the stage: - obtaining the data and offering recommendations for sorbent supply through organization of additional nozzles; searching for the optimal location of the nozzles and optimal consumption of the sorbent; and estimation of the importance of different factors influencing SO₂-removal efficiency.

Results and Discussion

Basing on the results obtained from preliminary calculations of motion trajectories of the sorbent particles (CaO) and on chemical reaction, the location of additional nozzles for TP-17-LTV boiler (Fig. 5) was adapted at the back screen of the combustion chamber at the level 2 m higher than the heating surface bend. The nozzles are evenly spaced along the combustion chamber screen to ensure a uniform filling of the interior space of the furnace with sorbent. The calculations have shown that 4-6 sorbent nozzles are quite enough to increase SO₂-removal efficiency up to 85-90 %. The total sorbent consumption through all the nozzles was pre-assigned to be equal to 1.6 t/h and it has to be uniformly distributed between the nozzles. The calculations which were carried out at the boiler load 50 % of the nominal load and at a sorbent consumption of 2.2 t/h have demonstrated that SO₂-removal efficiency increases from 85 % up to 90.7 % with increasing the sorbent consumption.

To confirm the correctness of the location of additional nozzles analogous calculations were performed at sorbent consumption of 1.6 t/h

provided that the sorbent nozzles were installed at the level 6 m higher than the heating surface bend. The calculated SO_2 -removal efficiency was found to be 10-12 % lower at load 100 % of the boiler nominal load and about 11 % lower at load 50 % of the nominal load in comparison with the case when sorbent nozzles were settled lower.

Basing on calculations the sorbent consumption and optimum position of sorbent nozzles allowing to increase SO_2 -removal efficiency up to 90 % were recommended for TP-17-LTV boiler.

For TP-17 (direct-flow) boiler, it was decided to place additional nozzles at the back and front screens of the combustion chamber at the level 3 m higher than the bend of heating surfaces to guarantee the uniform filling of the interior space of the furnace with sorbent. Three nozzles at each combustion chamber screen were evenly spaced along the screens. At a total sorbent consumption of 1.6 t/h through all the nozzles, SO_2 -removal efficiency reached 48.3 % and 59.1 % at the boiler loads 100 % and 50 % of the nominal load, respectively.

The best results of SO_2 -binding for this type of boilers have been obtained at asymmetrical gas velocity field when simulating the boiler operation with a cut-off burner.

Calculations were carried out at sorbent consumptions of 3.2 t/h, 4.8 t/h and 6.0 t/h. The efficiency increased from 57-59 % up to 67.9-90.7 % and in this case the maximum value of binding was obtained at sorbent consumption of 6.0 t/h.

The calculations performed for the case when sorbent nozzles are placed at the level 7 m higher than the heating surface bend have demonstrated an increase in the SO_2 -removal efficiency value by 30-40 % compared to that obtained at the nozzles location at the level 3 m higher than the bend.

Consequently, the results obtained for TP-17 (direct-flow) boiler have shown that an increase in SO_2 -removal efficiency can be achieved with much more difficulties and even at the maximum sorbent consumption (6.0 t/h) the binding efficiency is lower than that for TP-17-LTV boiler.

The performed calculations have confirmed that the most significant factors which govern the SO_2 -binding process in the furnace of boilers are the fields of flue gas temperature and the residence time of sorbent particles in the reaction zone. The SO_2 -removal efficiency value in TP-17-LTV boiler is higher than that in TP-17 (direct-flow) boiler owing to the lower temperature level of flue gases in the furnace of TP-17-LTV boiler. In addition, the total residence time of sorbent particles in the reaction zone of TP-17-LTV boiler furnace is longer than that in TP-17 boiler furnace.

One of the main factors affecting ash and sorbent particle residence time in the furnace chamber and governing the total value of SO_2 -removal efficiency is the field of flue gas velocities. Taking into account

the fact that the field of flue gas velocities in the furnace of TP-17 (direct-flow) boiler was pre-assigned approximately, further improvements prove to be feasible only on the basis of additional experimental and calculation research aimed at finding reliable initial data.

An increase in the residence time of fuel and sorbent particles in the boiler furnace tends to a rise in the particle concentration which is up to 0.3-0.5 kg/m³ in TP-17-LTV boiler. In this case the particles occupy the whole space of the furnace below the burners. In TP-17 (direct-flow) boiler the particle concentration is 10-100 times lower. However, the particle concentration influences the SO₂-removal efficiency to a lesser degree than flue gas temperature and reaction time.

SO₂-removal efficiency of a sorbent depends largely on the sorbent properties such as sorbent particle size distribution, reaction surface area and kinetic parameters [3-5]. In this work, the average values of kinetic parameters and reaction surfaces for separate particles were used and therefore the role of these factors has not been studied.

To obtain data on optimum fractional composition of the sorbent and its kinetic parameters additional calculations and experimental investigations are needed and this work is in progress.

SO₂-removal efficiency and sorbent consumption value depend to a large degree on location of the place of sorbent entry into the furnace. Correct placing of additional sorbent nozzles allows to achieve better results at decreased values of sorbent consumption. Calculations revealed that the replacing of additional nozzles greatly changes the value of SO₂-removal efficiency.

Experimental Testing of Calculation Results

Considering that just about 5 % of initial CaO may react in the boiler furnace it would be reasonable to use cyclone ash as an initial material for sorbent production. It corresponds to positive results obtained at a laboratory equipment [6]. The cyclone ash fractions with particle size over 200 μm contain the highest quantity of free CaO. So, it was recommended to supply previously milled cyclone ash into the boiler furnace through 6-8 sorbent nozzles to ensure a uniform overall filling of the interior furnace space with the sorbent. The sorbent consumption considering the amount of free CaO in the cyclone ash is 4-12 t/h for TP-17-LTV boiler and 11-30 t/h for TP-17 (direct-flow) boiler. The flow rate of transporting air and cross-section of the nozzles must ensure the velocity of sorbent entry not less than 20-25 m/s.

At the present time the works on designing and testing of a pilot-plant equipment for SO₂-removal from flue gases pioneered by the State

Enterprise *Eesti Energia* are in progress at the Baltic Thermal Power Plant (Narva, Estonia).

Conclusions

1. Generalization and analysis of the experimental data on flue gases vented to the atmosphere from oil shale burning boilers have shown that SO_2 concentration in flue gases of all the types of boilers increases with the growth of boiler steam load. SO_2 -removal efficiency depends on the type of boiler: TP-17 (direct-flow) boilers have the lowest SO_2 -removal efficiency and TP-101 boilers have the highest one. The data on SO_2 concentration in flue gases can be satisfactory generalized as a function of the boiler furnace heat liberation (q_v): $\text{SO}_2 = 0.0165 q_v$.
 2. A program complex basing on created mathematical models has been developed that allows to carry out the calculation of the efficiency of SO_2 -removal by oil shale ash components and by additional sorbents based on CaO. Some specific properties of the oil shale ash should be taken into account as well.
 3. Application of some sorbents based on ash-slag wastes of Estonian power plants were the most interesting solution. However, for lack of some data for properties and chemical activity of these substances, the application of a numerical analysis to the process with such kind of sorbent is difficult. So, it is necessary to continue the investigation of characteristics of the ash-slag wastes.
 4. Test calculations have shown that the program complex allows to follow the influence of the main factors on the SO_2 -removal process such as:
 - Gas temperature
 - Particle concentration
 - Interaction time
 - Particle size distribution
 - Particle structure
 - Place of the installation of additional sorbent nozzles, etc.
- A sufficiently well coincidence between calculated values of SO_2 -removal efficiency and experimental investigation data for TP-17 boilers has been obtained and the total value of SO_2 -removal efficiency is in the range from 42 to 74 %.
5. The analysis of the calculation results has revealed that there are significant possibilities to increase the SO_2 -removal efficiency by

injecting a previously activated additional sorbent into the furnace volume.

Engineering offers on the creation of a pilot-plant equipment for milled oil shale ash supply into the vortex zone of TP-17-LTV boiler have been developed. At present the works on mounting and testing of the equipment are in progress at the Baltic Thermal Power Plant (Narva, Estonia).

Nomenclature

C^* - dimensionless SO_2 concentration on the reaction surface

ψ - structural parameter

β - diffusion-kinetic parameter

Z - ratio of volume of solid phase after reaction to that before reaction

α - total conversion CaO into CaSO_4

α' - the part of the conversion CaO corresponding to reaction surface co-ordinate

τ - dimensionless time

t - time, s

T - temperature, K

σ_0 - radiation constant

ε - coefficient of "gas flow-particle" system radiation in the furnace

q_v - furnace heat liberation, kW/m^3

Nu - Nusselt number

λ - thermal conductivity, $\text{W}/(\text{m}\cdot\text{K})$

c_p - heat capacity of particle, $\text{J}/(\text{kg}\cdot\text{K})$

δ - size of sorbent particle, m

ρ - density, kg/m^3

m - mass, kg

Subscripts: p - particle; g - gas

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Presented by *V. Proskuryakov*

Received June 26, 1996

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A plasticizer obtained from high-sulfur shale oil (S content 6.5 %) was investigated as an additive for rubber compounds in quantities of 15 and 30 % on medium-high acrylonitrile-butadiene rubber, in comparison with dioctyl phthalate (DOP). The chemical composition of the shale oil additive was studied by chemical and spectral methods. The shale oil additive consisted mainly of compounds $C_{17}-C_{20}$, about 40 % of the total content consisted of sulfur compounds, mainly heavy derivatives of thiophene. The shale oil additive contained 45 % polar groups. The sulfonated compounds, as opposed to DOP, are likely to interact with the rubber chains. However, high content of sulfur compounds in the additive does not lead to chemical interaction with a vulcanized rubber. After compounding, the tensile strength and tear resistance of vulcanized rubber containing the shale oil additive were higher than those of the control. Repressive flexibility modulus of the vulcanized rubber containing the shale oil additive was lower, but rubber compounds had better properties of water absorption, resistance to the attack of microorganisms.

Introduction

Oil shales are one of the largest prospective sources of natural gas, coal in the world and are the most important national source of energy in Israel. Its reserves (20 billion tons) are enough to organize a large scale production of chemicals, much of which belongs to the family of high-sulfur fuels. Deposits of high-sulfur oil shales are found in many