ANATOLIY IVANOVICH KOBJAKOV
IGOR MIHAYLOVICH ARPISHKIN

Moscow State University of Environmental Engineering, Moscow, Russia

SCIENTIFIC PAPER

661.25.00.645

CONTACT OXIDATION OF CONCENTRATED SO_2 MIXTURES – II, Different types of catalyst layers connection

In part – II of the work the factors affecting the controllability of contact oxidation of concentrated SO_2 mixtures were determined. Different connection circuits of the reactor contact layers were considered and a comparative analysis of the technological circuit carried out.

CIRCUITS OF CONNECTIONS OF CONTACT MASS LAYERS

The important aspect of the problem of concentrated mixture oxidation in a multilayer plant is the structural arrangement in relation to the inlet and outlet gas flows. To achieve the highest specific capacity of a multilayer contact plant, a reactive gas of the composition necessary to obtain the maximum specific capacity has to be fed to every layer inlet. This means that the reactive load must be distributed along the layers of the contact plant and SO_3 be absent from the reactive gas fed to each layer. Since SO_3 must be absent in the original mixture, then with the in–series connection of the layers of the contact plant (Fig.1) used for an air–gas mix–processing, uniform loading of the reactive layers is not realizable and SO_3 evolution from the interlayer contact gas requires the availability of extra–equipment.

When the layers are connected in–series, the absence of sulfur trioxide in the reactive mixture is possible for the first layer only. Therefore, from the standpoint of the contact mass specific capacity, a single–layer contact plant (Fig. 2) is more preferential. However, the essential disadvantage of a single – layer plant is the high extent of recirculation and the complexity of control over the temperature. In such a circuit, the magnitude of recycling is of the order of 85% of the reactive gas volume fed to the plant. In this case, variations of the reactive gas consumption and composition can result in contact mass overheating.

The extent of recirculation can be decreased and the temperature control in the contact mass layer improved by the use of a parallel connected circuit (Fig. 3). Under this structural organization of the contact plant, the presence of some amount of SO_3 is inevitable at the inlet of the layers. However, the ability of SO_3 to slow down the rate of SO_2 oxidation exerts a positive effect on the layer; the presence of SO_3 increases the

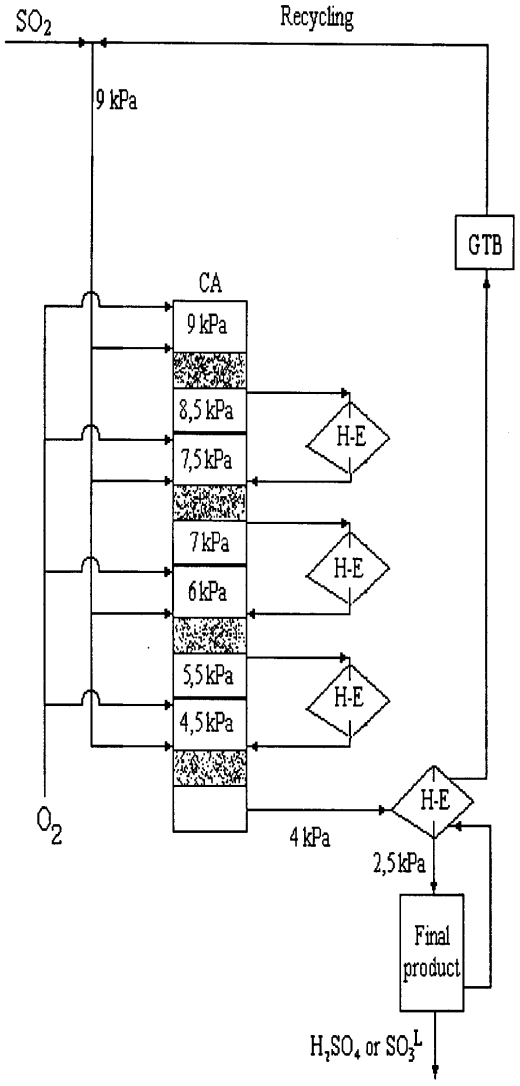

Figure 1. In–series circuit of contact oxidation process of concentrated SO_2 mixtures

Author address: A.I. Kobjakov, Moscow State University of Environmental Engineering, 21/4 Staray Basmannaya St., 107884 Moscow, Russia; E–mail: msace@rinet.ru
Paper received: July 8, 2000
Paper accepted: December 11, 2000

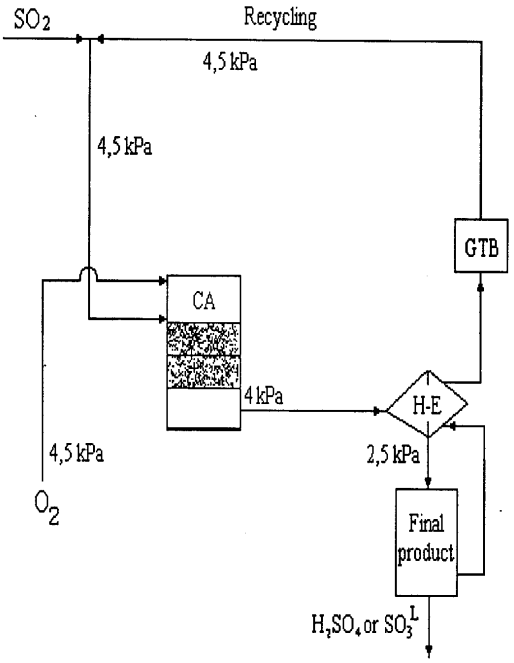

Figure 2. Single layer contact plant for the contact oxidation process of concentrated SO_2 mixtures

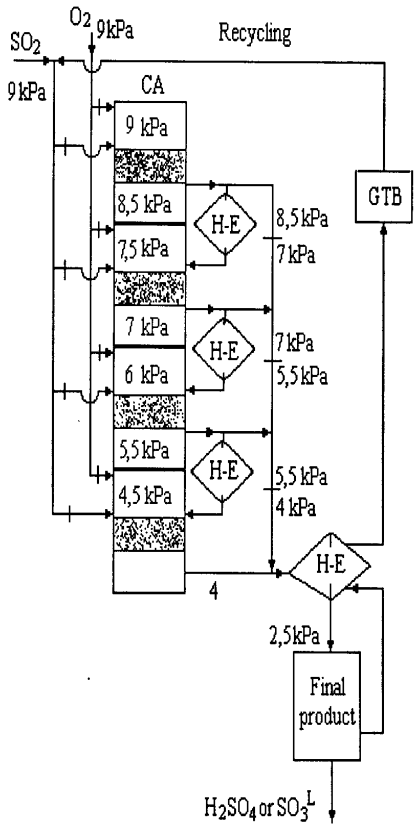

Figure 3. In parallel circuit of the contact oxidation of concentrated SO_2 mixtures

theoretical time of contact and ensures its value is bigger than the actual contact time, which prevents catalyst overheating. This method artificially brings the gas to the equilibrium composition and, as in the classical circuit (in–series connected layers) used for the processing of gas–air mixtures, allows some reserve of contact mass, in case of catalyst activity, to be built up in the layer.

In an in–parallel circuit, a portion of the gas flow from the preceeding layer outlet is fed to the inlet of the subsequent one. The remaining flow is fed to the general point of SO_3 release. From the last layer outlet, the entire flow is fed to the point of SO_3 release and the required amount of SO_3 is fed to the first layer of the plant through the recycling. The controlling effect on the amount of SO_3 in the reactive gas and, as a result, on the layer temperature condition, is the degree η of gas flow splitting – the relation of the magnitude of contact gas flow fed to the SO_3 release point to the magnitude of flow released from the layer.

Consider in greater detail the nature of the control over the temperature condition of the layer. The layer temperature condition is affected by both the reactive gas composition and it consumption. A change in the reactive gas composition result in a change in the quantity of the theoretical time contact which result from $dNi/dl = \nu_i \cdot R \cdot S$ (see eq. (2), [1]) after substitution of $dl = d\tau \cdot G/S$ and rearrangement followed by integration:

$$\tau^{th} = \frac{1}{G} \int_{N^0_{SO_3}}^{N^f_{SO_3}} \frac{1}{W} dN_{SO_3}, \qquad (1)$$

In turn, the consumption of the reactive gas affects the value of the real contact time

$$\tau^{tr} = V / G. \qquad (2)$$

In a classical circuit $\tau^{tr} = \chi \cdot \tau^{th}$. The factor χ, used from interval (1–4), determines the reserve in the contact mass layer [2]. When $\chi > 1$, then $\tau^{tr} > \tau^{th}$. In this case the processing of concentrated mixtures within the limits of the specified temperature condition (refer to (5)–(7), [1]) is limited by the concentration of one of the reagents or by the presence of some sulfur trioxide in them, at the cost of which the contact gas at the layer outlet is close to the equilibrium composition. Such mixtures are like mixtures 2, 13–17 of Table 1.

During oxidation of the concentrated mixtures 3–12 and in the case of $\chi > 1$, contact mass overheating is inevitable. For mixtures like 3–12 it is essential that the value of χ should meet the condition $\chi \leq 1$. Consider an example. Set $\chi = 1$. What would occur if, for example, the reactive gas consumption undergoes a change?

In the case that the gas consumption increases, the real contact time will decrease, the theoretical contact time will remain as before and $\tau^{tr} < \tau^{th}$. This being so, the capacity of the layer and the temperature of the gas at the layer outlet will decrease. In the case that the reaction gas consumption decreases, the real contact time will increase and become longer than the theoretical contact time. In the end the temperature of

Table 1. Specifications of sulfuric mixture oxidation process in the contact mass adiabatic layer (N = 100 mole/s, T^o = 72 3 K, T^f = 873 K)

Srl No	Mixture composition, % vol.				Fractional conversion		V	Ω	ω
	SO_2	O_2	SO_3	N_2	X^o	X^f	m^3	mol/s	mol/($s \cdot m^3$)
1	9.0	12.0	0.0	79.0	0.724	0.737	24.36	6.721	0.290
2	9.24	90.76	0.0	0.0	0.886	0.899	4.125	8.310	2.014
3	13.0	87.0	0.0	0.0	0.650	0.897	2.713	8.640	3.147
4	15.0	85.0	0.0	0.0	0.560	0.896	2.685	8.660	3.223
5	16.6	83.4	0.0	0.0	0.510	0.895	2.713	8.760	3.229
6	19.0	81.0	0.0	0.0	0.450	0.893	2.769	8.820	3.185
7	23.0	77.0	0.0	0.0	0.380	0.890	2.854	9.0	3.153
8	43.0	57.0	0.0	0.0	0.220	0.865	4.041	9.650	2.388
9	53.0	47.0	0.0	0.0	0.180	0.841	5.030	9.860	1.965
10	63.0	37.0	0.0	0.0	0.160	0.790	6.585	10.019	1.522
11	73.0	27.0	0.0	0.0	0.140	0.655	9.608	10.750	1.119
12	85.5	14.2	0.0	0.0	0.120	0.332	19.50	10.760	0.552
13	94.6	5.4	0.0	0.0	0.113	0.114	110.2	10.750	0.098
14	14.4	65.6	20.0	0.0	0.879	0.882	13.85	10.340	0.747
15	16.9	55.1	28.0	0.0	0.867	0.870	19.49	11.150	0.572
16	17.7	52.3	30.0	0.0	0.865	0.867	21.19	11.400	0.538
17	37.6	12.8	49.6	0.0	0.721	0.781	89.02	13.400	0.151

the contact gas at the layer outlet will increase and exceed the allowable value; there exists a great danger of contact mass overheating.

At the same time, perturbations, associated with variations in the reactive mixture consumption, can be compensated for by changing the mixture composition. By changing the relation SO_2:O_2 or the content of SO_3 in the reactive mixture, the theoretical contact time within the contact mass volume can be changed.

For instance, once the gas consumption has increased, then, to perform under a specified temperature condition (ref. To (5)–(7), [1]) and to maintain the capacity, either the SO_3 content must be reduced by increasing η, the division of the contact gas flow at the layer outlet, or the SO_2:O_2 ratio must be changed by increasing the content of O_2 in the reactive gas.

Note that a change of the SO_3 content of the reactive gas has a stronger action upon the contact mass volume and, hence, upon the value of the theoretical contact time than a change of the relation SO_2:O_2 (ref. to Fig.4–5, [1]).

Moreover, a change of the amount of sulfur dioxide in the reactive gas is limited by the power (capacity) and sluggishness of the furnace section. Consequently, it makes sense to vary the SO_2:O_2 ratio and η to control τ^{th}. The reactive gas providing the lower limit of τth corresponds to such a composition wherein the contact mass volume is minimal. In particular, this composition is (% vol.): SO_2=15, O_2=85. In this case τ^{th} = 0.45 s. Any change of the composition is followed by an increase in the theoretical contact time. Changing of gas composition [(SO_2=9.24, O_2=90.76); (SO_2=15, O_2=85)] allows the consumption to be changed 1.54 times. For [(SO_2=94.6, O_2=5.4); (SO_2=15, O_2=85)] the gas consumption change can be 41 times.

An addition of a small amount of SO_3 at the layer inlet markedly extends the limit of possible change of gas the consumption through the layer. So, the presence of 5% volume of SO_3 in the reactive gas with SO_2:O_2=17.9:82.1 allows the theoretical contact time to be increased 1.44 times and reactive gas consumption to be decreased by as many times. In the case of 10% of SO_3 with the same SO_2:O_2 ratio, τ^{th} increases 2.04 times.

In the analyzed circuit, it is simple enough to alter the composition and consumption of the reactive gas at the layer inlets and make an invariant change of these parameters over a wide range of values. This advantage is due to the possibility of feeding concentrated sulfuric gas and oxygen into every layer by means of independent flows. In its turn, the division of the contact gas at the outlet from each layer into two flows, one of which is fed to the location where the final product (H_2SO_4, SO_3 liquid) is obtained in an absorber or a condenser–refrigerator common for all the layers and the other is fed to the next layer, a condition neccesary for the achievement of a high specific capacity of the contact mass layer.

When a single–layer contact plant is compared with a 4–layer one in which layers are connected in–series and in–parallel, attention must be drawn to the fact that the efficiency indices considered – capacity, specific capacity and contact mass volume – depend on the analogous indices of every layer. The given indices and their dependence on the reactive gas composition, as applied to the layer, have been analyzed in Part I.

Thus, in this paper, the main attention is focused on the magnitude of recycling and also on the energy expenditure E_r for transferring the gas in the system (overcoming pressure friction loss) and on the energy E_O for obtaining oxygen. The results of the calculations are given in Table 2. From these data it follows that the contact mass volume and the reactive gas consumption for different circuits change markedly. At the same time, the capacity of the circuits under consideration (except for the classical circuit without recycling) change over a small range from 33 to 41 mol/s of sulfur trioxide. This gives ground to compare (with some error) the gas consumption through the contact system of interest and the energy expended for the gas transfer of all the circuits considered, the reactive gas consumption (400 mol/s) is maximal for a single–layer plant and contact mass volume (10.85 m^3) is minimal. The capacity of this single–layer circuit is 35 mol/s of sulfur trioxide.

The capacity of 4–layer in–series and in–parallel circuits ranges from 33.8 to 40.5 mol/s. For 4–layer

Table 2. Efficiency indices of the contact apparatus

Connection structure of layers	V	Ω	ω	N	Recycling	η	E_r	E_o
	m^3	mol/s	mol/(s · m^3)	mol/s	mol/s		kJ/s	kJ/s
In–series	36.74	40.54	1.103	100.0	39.2	0.0	53.39	524.7
In–series with SO_2 distribution	48.98	46.50	0.95	170.3	96.4	0.0	88.72	601.9
In–parallel	70.54	43.16	0.61	201.3	136.6	0.3	107.5	558.7
In–parallel	32.55	36.88	1.133	257.4	201.6	0.5	137.4	477.4
In–parallel	22.16	35.00	1.580	313.9	261.5	0.7	167.6	453.0
In–parallel	18.31	33.76	1.863	370.9	324.5	0.9	198.1	437.0
Double layer in – parallel	32.55	36.88	1.133	257.4	201.6	0.5	91.6	477.4
Single layer	10.85	35.04	3.229	400.0	347.4	0.0	106.8	453.6
Classical	77.0	8.98	0.120	100.0	0.0	0.0	53.39	0.0

contact plants with recycling, the reactive gas consumption through the system decreases when η is reduced, therefore the energy required for the transferring gas through the system is reduced.

On the other hand, the expenditure of energy for transferring gas through the system is increased because of the pressure loss in the system. Using the data given in [2], the layer pressure loss is assumed to be 0.5 kPa, the heat–exchanger pressure loss 1.0 kPa, and the release unit pressure loss 2.5 kPa. The recycling pressure loss is ignored because of its insignificance.

Calculations show that the pressure loss of in–series and in–parallel 4–layer circuits does not exceed 10 kPa. For a single – layer circuit this parameter is minimal and equal to 4.5 kPa. The overpressure changes along the movement of the gas flows are shown in Figs. 1–4. A peculiarity of the in–parallel circuit lies in the necessity of mounting a large number of control units on the pipelines distributing oxygen and sulfurous gas along layers of the contact plant and on the pipelines for discharging the contact gas from the system.

The expenditure of energy for the transference of gas depends on the pressure loss of the system and voluminal gas consumption:

$$E_r = G \cdot \Delta P \qquad (3)$$

This expenditure for a 4–layer in – parallel circuit is from two to four times larger than that for an in–series circuit. The expenditure E_r can be reduced mainly by decreasing the height and number of the contact mass layers. The double–layer in–parallel circuit is shown in Fig. 4. Its pressure loss is not higher than 6.0 kPa, the expenditure of energy necessary to overcome this pressure loss is 91.6 kJ/s; the remaining efficiency indices are identical to those for the 4–layer in–parallel circuit.

In a double – layer circuit, the energy expenditure for transferring gas along the system does not exceed that of a single – layer circuit, is virtually equal to that for

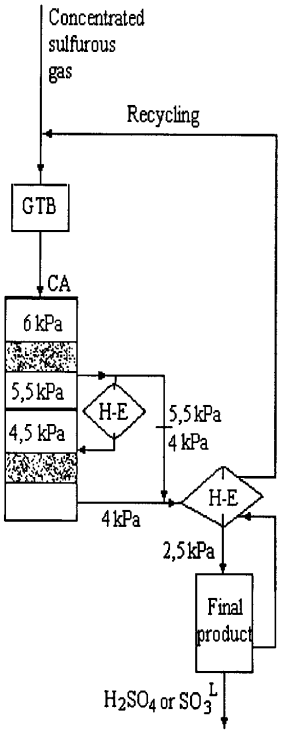

Figure 4. Double–layer in–parallel circuit

the in–series circuit with SO_2 distribution and is nearly twice as large as that for the series circuit without SO_2 distribution along the layers. An increase in the amount of recycle gas of the circuits under consideration takes place in the same order. The least gas is recycled in the in–series circuit without sulfur dioxide (sulfurous gas) distribution. Next are the in–series circuits with sulfur dioxide distribution, the double–layer in–parallel, the 4–layer in–parallel and the single–layer circuits. Hence, it follows that the energy expenditure E_r is substantially affected by the amount of gas recycled and, to a lesser extent, by the pressure loss in the system.

Oxygen and kiln gas are fed to the contact section under an overpressure 0.01–0.06 MPa. This pressure is

quite sufficient for transferring gas through the contact plant. Thus, one gas turbo–blower is sufficient in the circuit with recycling.

To the concentrated sulfide mixture flowsheet, the energy expenditure for obtaining oxygen must be added to the energy expenditure for overcoming pressure losses.

For instance, 75 mol/s of oxygen is required to obtain 50 mol/s of sulfur trioxide. To obtain that amount of oxygen, no less than 354 mol/s of air must be cooled to 80 K. The expenditure of energy for this operation will be $E_O = N \cdot R \cdot \Delta T = 354 \cdot 8.31 \cdot (300–80) = 647.2$ kJ/s. At the same time, while burning 50 mol/s of sulfur, 4.6 MJ/s of heat is liberated. The present–day heat – recovery systems are *no* less than 50% efficiency. This means that the excess heat generated during the oxidation of S to SO_2 is sufficient not only to obtain the required oxygen, but also to compensate for the operating expenditure of a cyclic circuit. Consequently, the operational expenditure cannot be a counter argument of mastering cyclic circuits for the processing of concentrated sulfide mixtures.

The capital outlays for the construction of an air–separating unit which affect the cost of cyclic flow chart products and the payback time of sulfuric acid manufacture are the issues which compromise the selection of the productive capacity. However, pinpointing a solution to this is a design problem.

Mastering in–parallel cyclic circuits, which combine a high capacity of the contact mass layers with reliable control over the contact plant thermal condition, opens new prospects and possibilities for introducing ecologically perfect sulfuric acid units. The performed analysis of the process of the oxidation of concentrated sulfide mixtures performed, the diagrams of the structural organization considered and the aspects of control over the contact plant established are subject to the resolution of the issues connected with the creation of ecologically clean and economically effective automated circuits.

DESIGNATIONS

E – expenditure of energy, J/s;
L, *l* – height of the contact mass layer and its current coordinate, m;
G – gas rate consumption, m^3/s;
N, N_i – molar rate of reactive mixture and the ith– component, mol/s;
P, P_i, ΔP – total pressure and partial pressure of ith–component, Pa;
R – gas constant, $J/(K \cdot mol)$;
S – cross–section area of the contact mass layer, m^2;
T, ΔT – temperature and temperature drop, K;
V – volume of the contact mass layer, m^3;
r – chemical reaction rate, $mol/(m^3 \cdot s)$;
τ – contact time of reaction mixture with catalyst, s;
η – splitting coefficient of the flow;
χ – coefficient of contact mass store;
ν_i – stoichiometric coefficient of reaction for the ith–component;
i $\in$ { SO_2, O_2, SO_3 }.

Superscripts:

f – at layer output;
0 – at layer input;
th – theoretical value;
tr – true value.

Subscripts:

r – pressure loss;
o – oxygen.

REFERENCES

[1] Kobjakov A.I., Arpishkin I.M. Contact oxidation of concentrated sulfide mixtures–I, Chem. Ind. 54 (2000) 546.
[2] Sulfid acid worker reference book – Moskow: Chemistry, 1971, p. 559–570.

IZVOD

KONTAKTNA OKSIDACIJA KONCENTROVANIH SMEŠA SUPORNIH OKSIDA – II,
Uticaj različitog načina povezivanja katalitičkih slojeva

(Naučni rad)

Anatoliy Ivanovich Kobjakov, Igor Mihaylovich Arpishkin
Moskovski državni univerzitet za inženjerstvo zaštite životne sredine, Moskva, Rusija

U drugom delu ovog rada analizira se uticaj faktora koji kontrolišu oksidaciju koncentrovanih gasovitih smeša sumpor dioksida. U radu se analiziraju različite mogućnosti povezivanja slojeva katalizatora i izvodi se njihova uporedna analiza.

Ključne reči: Oksidacija sumpor dioksida • koncentrovane smeše • višeslojni reaktor • način povezivanja •
Key words: Oxidation of sulpfur dioxide • Concentrated mixtures •