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DESULPHURIZATION OF GAS BY SORPTION OF SULPHUR DIOXIDE ON CUPRIC OXIDE DEPOSITED ON ALUMINA PARTICLES IN A FLUIDIZED BED REACTOR

This work concerns the desulphurization of air, sulphur dioxide, nitrogen dioxide, carbon dioxide and water mixtures by chemical sorption of sulphur dioxide on cupric oxide deposited on porous alumina particles. Gas and solids flow countercurrently in a multistaged fluidized bed reactor. Cupric sulphate resulting from the reaction is then reduced by methane.

Effects of gas and solids flow rate, residence time of solids in the reactor, temperature, and sulphur dioxide and other gases concentrations have been studied. Desulphurization yields exceeding 90% have been obtained in the four-stage reactor and sulphur dioxide concentration can be reduced from 3000 ppm to less than 300 ppm with a small gas pressure drop.

NOTATIONS

C_e – inlet sulphur dioxide concentration (ppm),
C_i – outlet sulphur dioxide concentration for stage i (ppm),
L – downcomer height (mm),
Q_G – gas flow rate ($N\,m^3h^{-1}$),
Q_s – solid flow rate ($kg\,h^{-1}$),
T – reactor temperature (°C),
T_i – stage i temperature (°C),
T_{ge} – inlet gas temperature (°C),
T_{po} – inlet solid temperature (°C),
Y_i – desulphurization yield of stage i (%),
Y_G – total desulphurization yield (%).

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1. INTRODUCTION

Among the flue gas desulphurization processes studied presently or being in operation, those using reactions of sulphur dioxide with solid metal oxides are of particular interest [5]. These processes are carried out at temperatures ranging within 300–400°C, which corresponds to usual temperatures of flue gas. However, the sulphates formed are sometimes difficult to decompose. To avoid this difficulty manganese oxide, alkalized alumina, or cupric oxide may be used, provided that the mechanical strength of solid particles is high enough to prevent dust pollution, and the gas pressure drop is small. An example of this kind of processes is the Shell process [4] in which two fixed bed reactors operate alternatively in sorption and regeneration at the same temperature (300–400°C). Then the reaction:

$$CuO + 1/2O_2 + SO_2 \rightarrow CuSO_4$$

is slightly exothermic. The cupric oxide is deposited on porous alumina particles. It should be noted that if the copper concentration is not sufficiently high (less than 3 %), other compounds resulting from the reaction of sulphur dioxide with alumina appear and the activity of the solids decreases. Then the sulphate formed is reduced at the same temperature by methane or carbon monoxide and hydrogen mixtures into copper which is easily oxidized by oxygen:

$$CuSO_4 + 1/2CH_4 \rightarrow Cu + 1/2CO_2 + H_2O + SO_2.$$

The exit gas from the regeneration reactor contains about 30–35 % of sulphur dioxide. It can be either treated in a CLAUS unit to produce sulphur or oxidized into sulphur trioxide on a catalyst and then transformed into sulphuric acid.

The Shell process is not really continuous. Each cycle takes 1 h. Therefore this reaction can be conveniently carried out in a fluidized bed reactor. The main advantage of this procedure is to make the operation continuous and the exit sulphur dioxide concentration constant. In a one stage reactor, BARRETEAU [1] obtained a 50 % desulphurization yield. Using model simulation, he predicted that in a four-stage reactor desulphurization yields might be higher than 90 %. The present work has been undertaken in order to verify this prediction. The effects of water, carbon dioxide and nitrogen oxide concentrations on the desulphurization yield have also been studied.

2. APPARATUS

The apparatus is shown schematically in fig. 1. It has been described in full detail elsewhere [3], [6]. The reactor is made of refractory steel. Four stages 150 mm high and 98 mm in diameter are stacked vertically. The distributor

for each stage is a perforated plate. Solids flow down from one stage to the other through downcomers. Pressure gauges, thermocouples, gas and solids sampling valves are provided. Solids, added from a hopper, and gas mixtures are preheated in two fluidized beds before being fed into the reactor. Gas mix-

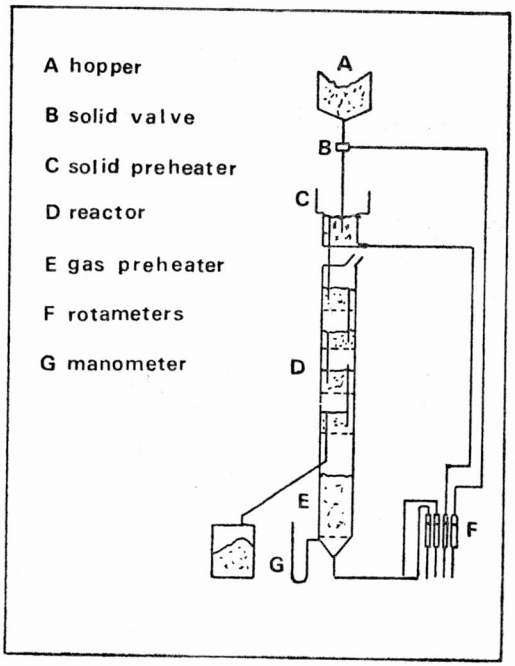

Fig. 1. Desulphurization unit
Rys. 1. Urządzenie do odsiarczania

tures are analysed either by gas chromatography or infrared spectrometry. A commutating valve selects the gas samples from different stages. Solids leaving the reactor are stored and regenerated periodically in another reactor by a reaction with methane.

3. PREPARATION AND ANALYSIS OF THE SOLID

Alumina particles are first sieved and dried. Thereupon they are immersed in an aqueous copper sulphate solution (0.76 mole/dm^3) and dried at 80°C. The sulphate is reduced by methane in the regeneration reactor and the product is oxidized in air at 300°C to give copper oxide. The physical properties of the solid are presented in tab. 1. The analyses of solids for determining sulphur sulphate and copper contents have been carried out by „Société Nationale ELF AQUITAINE".

4. EXPERIMENTS – RESULTS

The desulphurization yield is defined as:

$$Y_G = \frac{C_e - C_i}{C_e}$$

where C_e and C_i are the respective inlet and outlet concentrations of sulphur dioxide in gas.

Thus for stage i we have:

$$Y_i = \frac{C_{i+1} - C_i}{C_{i+1}}$$

where C_i and C_{i+1} are the outlet and inlet sulphur dioxide concentrations, respectively, for the stage. These yields depend on the gas flow rate Q_G, the solids flow rate Q_S, the solids residence time in each stage, defined in terms of the height of the downcomer L, temperature T, and the water vapour, carbon dioxide and nitrogen dioxide concentrations.

Table 1

Physical properties of the sorbent
Fizyczne właściwości sorbenta

Property	Value
Density	1600 kg m^{-3}
Particle diameter	400 μm
Minimum fluidization velocity at 20 °C	0.30 m s^{-1}
Specific area of unreacted sorbent	184 m^2g^{-1}
Specific area of SO_2 saturated sorbent	161 m^2g^{-1}
Mean pore diameter	55Å
Weight fraction of copper	3.77–4.12%

The first series of experiments, carried out at a temperature of 300°C and an inlet sulphur dioxide concentration of 2000 ppm, was concerned with the effects of the first three parameters on the desulphurization of air–sulphur dioxide mixtures. The experiments were performed according to a 2^3 factorial design. The experimental conditions lead to a mean residence time for solids between 6 and 30 min, gas velocity between 0.77 and 1.4 m/s. Thus contact times between solid and gas were between 0.08 and 0.3 s. In order to determine the experimental error variance, the experiment was repeated four times for the average values of the three parameters. The results are presented in tab. 2.

The yield was always above 48 %, and it could be as high as 98 %. Gas pressure drop was less than 140 mm water, the outlet sulphur dioxide concentration less than 1000 ppm and usually less than 300 ppm. It should be noted that in France the maximum allowable sulphur dioxide concentration is about

Table 2

Effects of gas and solid flow rates and height of downcomers on desulphurization yields
Wpływ prędkości przepływu gazu i ciała stałego oraz wysokości przewodu opadowego na wydajność odsiarczania

Run No.	101	102	103	104	105	106	107	108	109	110	111	112
Q_s (kgh^{-1})	2	5	2	5	2	5	2	5	3.5	3.5	3.5	3.5
Q_g (m^{3}h^{-1})	10	10	18	18	10	10	18	18	14	14	14	14
L (mm)	30	30	30	30	60	60	60	60	45	45	45	45
C_e (ppm)	1950	1924	1924	1933	1927	1965	1973	1998	1903	1888	1922	1913
T_{ge} (°C)	297	298	293	292	298	297	291	295	296	293	294	294
T_{Po} (°C)	375	314	376	328	380	380	346	340	350	354	360	360
C_1 (ppm)	273	42	998	568	95	30	705	243	250	265	294	200
C_2 (ppm)	636	140	1316	932	370	50	1135	558	647	710	755	592
C_3 (ppm)	910	330	1494	1195	798	184	1465	1000	978	1038	1097	942
C_4 (ppm)	1381	902	1694	1557	1212	567	1706	1402	1355	1400	1450	134
T_1 (°C)	303	300	299	300	298	305	300	303	306	307	306	305
T_2 (°C)	298	297	302	302	295	292	302	293	304	304	301	302
T_3 (°C)	301	300	304	303	300	292	303	300	306	304	303	304
T_4 (°C)	306	306	305	306	308	305	308	306	310	306	306	307
Pressure drop (mm H_2O)	84	84	86	86	125	140	131	146	93	93	93	93

1400 ppm, while in other countries, like the U.S.A., Japan or Germany, it is about 350 ppm. If the solids flow rate was suitably chosen, the exit sulphur dioxide concentration would fall down below 300 ppm. It may also be observed that the mechanical strength of the solid was good. This was confirmed by comparing the particle size analyses made before and after 150 h operation. It seems that the presence of copper renders the alumina particles more resistant to attrition [1], [6].

If we compare the results of the experiments, we can see that the desulphurization yields are higher when the flow rate and residence time of solids are higher, and the gas flow rate lower. These observations have been confirmed by statistical analysis [6].

In a second series of experiments the effects of temperature (300–400°C) and of the inlet sulphur dioxide concentration (500–5000 ppm) were determined. The results are presented in tab. 3 and figs. 2 and 3. The reaction rate depends

on temperature [3], the desulphurization yield increases with temperature (fig. 2). The value of the yield Y_1 obtained in the first stage at 400°C is certainly wrong because of the error in measurement of C_1 and C_2 concentrations which in this case amount to less than 100 ppm. The total desulphurization yield approaches 100% at temperatures higher than 330°C.

Table 3

Influence of temperature and inlet sulphur dioxide concentration on desulphurization yields
Wpływ temperatury i wlotowego stężenia dwutlenku siarki na wydajność odsiarczania

Run No.	201	202	203	301	302	303	304	305	306
	Q_S = 3.5 kgh^{-1}			Q_G = 14m^{3}h^{-1}			L = 45 mm		
C_e(ppm)	1910	1924	1924	495	986	1500	2908	3963	4850
T_{ge}(°C)	326	351	398	290	289	290	291	297	294
T_{po}(°C)	330	435	480	347	367	353	348	350	340
C_1(ppm)	83	40	31	10	40	92	558	913	1583
C_2(ppm)	348	189	73	30	112	316	1267	2013	2950
C_3(ppm)	643	444	207	68	242	568	1692	2600	3608
C_4(ppm)	1130	957	650	158	480	902	2158	3200	4133
T_1(°C)	330	358	395	301	308	301	309	308	309
T_2(°C)	328	355	389	301	302	299	307	305	308
T_3(°C)	329	357	394	302	300	299	306	305	307
T_4(°C)	334	364	406	304	302	302	306	309	307
Pressure drop (mm H_2O)	99	98	96	98	101	97	101	105	101

Increasing inlet sulphur dioxide concentration affects the desulphurization yield adversely (fig. 3) due to an increase in the sulphate concentration, which results in a decrease of the sorbent activity. It should be noted that in all the experiments the first stage yield is always the higher because the solid which enters this stage does not contain any copper sulphate yet.

Finally, the third series of experiments was performed to assess the effect of carbon dioxide, nitrogen dioxide and hydrogen oxide concentration. Note that the effect of the oxygen concentration was not considered though it might be thought that it would affect the reaction kinetics. As only one stage of the reactor was used, the desulphurization yield was less than in the preceeding experiments. A factorial design was still chosen with carbon dioxide concentration between 11 and 17%, hydrogen oxide between 2 and 10%, and nitrogen dioxide between 100 and 150 ppm. The results were compared with those for

experiments without carbon dioxide, nitrogen dioxide and hydrogen oxide (tab. 4). Nitric oxide does not influence the desulphurization yield which in presence of carbon dioxide slightly decreases. The water vapour exhibits the strongest influence. This observation is confirmed by statistical analysis [2].

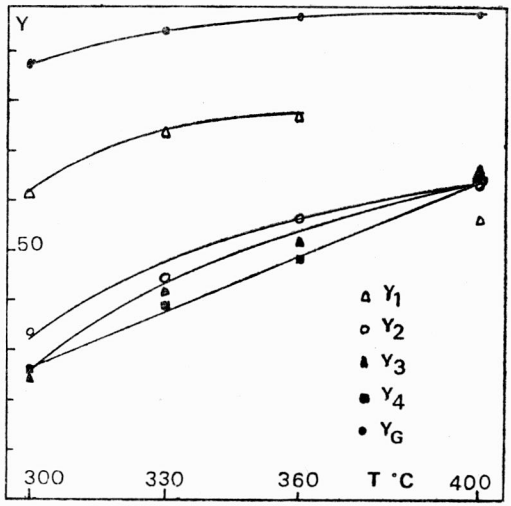

Fig. 2. Desulphurization yields versus temperature
Rys. 2. Wydajność odsiarczania w zależności od temperatury

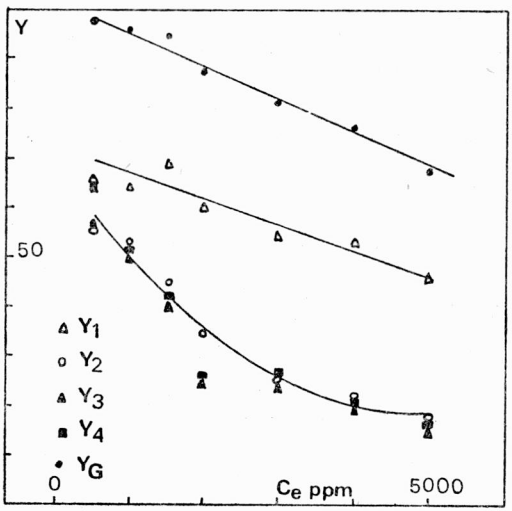

Fig. 3. Desulphurization yields versus inlet SO_2 concentration
Rys. 3. Wydajność odsiarczania w zależności od wlotowego stężenia SO_2

Table 4

Influence of nitrogen dioxide, carbon dioxide and water vapour concentrations on desulphurization yields
Wpływ stężenia dwutlenku azotu, dwutlenku węgla i pary wodnej na wydajność odsiarczania

Run No.	% (vol.) CO_2 %	% (vol.) H_2O %	C_e ppm NO_2	C_e ppm SO_2	T_{ge} °C	T_{pe} °C	T °C	ΔP cm of H_2O	C_1 ppm SO_2	Y_G %
P_1	11	2	100	2026	298	299	296	2.3	1114	45.0
P_2	17	2	100	2172	299	300	296	2.3	1279	41.1
P_3	11	10	100	2125	303	298	299	2.4	1296	39.0
P_4	17	10	100	2121	300	304	301	2.3	1379	35.0
P_5	11	2	500	2190	301	308	302	2.2	1204	45.0
P_6	17	2	500	1913	300	301	299	2.3	1088	43.1
P_7	11	10	500	2176	304	302	301	2.4	1284	41.0
P_8	17	10	500	2106	302	301	299	2.3	1326	37.0
P_9	14	6	300	1837	304	299	305	2.3	1186	35.4
P_{10}	14	6	300	1990	300	306	306	2.3	1278	35.8
P_{11}	14	6	300	1891	299	295	302	2.3	1186	37.3
P_{12}	14	6	300	1972	298	307	301	2.3	1195	39.4
S_1	0	0	0	2054	301	305	301	2.2	1161	43.5
S_2	0	0	0	1990	299	309	301	2.3	1240	37.7
S_3	0	0	0	1880	298	300	302	2.2	1031	45.2
S_4	0	0	0	2050	299	299	300	2.3	1177	42.6

Q_S = 3.5 Pag/h, Q_G = 6.67m³/h, L = 45 mm

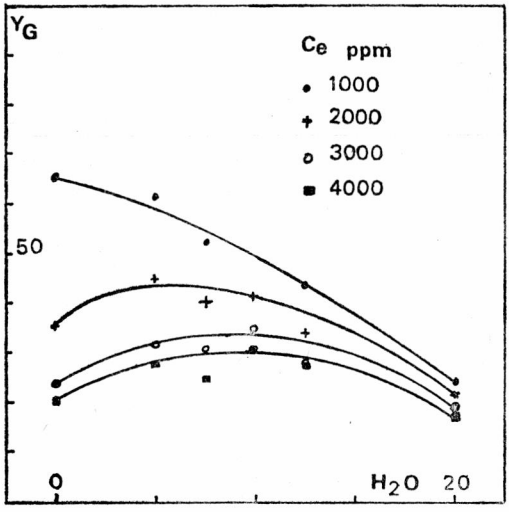

Fig. 4. Influence of SO_2 and water vapour concentrations on desulphurization yield
Rys. 4. Wpływ stężenia SO_2 i pary wodnej na wydajność odsiarczania

Carbon dioxide molecules are bigger than the others (N_2, O_2, H_2O), thus they can slow down the diffusion of sulphur dioxide in the pores of the solid and reduce the desulphurization yield. Other experiments were performed by using mixtures of air, sulphur dioxide and water. The results are reported in fig. 4. It can be noted that the yield achieves the maximum at water concentration between 6 and 10% except for sulphur dioxide concentration of 1000 ppm. At low concentrations, water seems to promote the desulphurization, but an opposite effect being observed at higher concentrations.

Influence of water concentration can be explained in two different ways:

1. As in corrosion of metals, which is enhanced by the presence of water, the oxidation of sulphur dioxide to sulphur trioxide is promoted by water vapour so that the sulphatation of copper oxide becomes faster.

2. Water can interact with alumina and copper sulphate to give hydrated salts. The blue–green colour of some particles tends to confirm this supposition. The hydration of the sorbent could reduce its activity.

These two opposed effects could explain the observed variations of the yield. For experiments at the lowest sulphur dioxide concentration, the second effect is more likely.

5. CONCLUSIONS

Desulphurization yields of more than 90% can be obtained by chemical sorption of sulphur dioxide on copper oxide deposited on porous alumina particles in a fluidized bed reactor working at about 300°C. The sulphur dioxide content of the exit gas can be reduced to less than 300 ppm. The gas pressure drop is not prohibitive and the mechanical strength of the solids is sufficient to avoid dust pollution. The presence of the other components in the flue gas leads to a slight decrease in the desulphurization yield. This could be compensated by a better choice of the operating conditions. The process could then be used to control sulphur dioxide pollution by flue gas.

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ODSIARCZANIE GAZU PRZEZ SORPCJĘ DWUTLENKU SIARKI NA TLENKU MIEDZI OSADZONYM NA CZĄSTECZKACH GLINU W REAKTORZE ZE ZŁOŻEM FLUIDALNYM

Omówiono odsiarczanie powietrza, dwutlenku siarki, dwutlenku azotu, dwutlenku węgla i mieszanin wodnych przez sorpcję chemiczną dwutlenku siarki na tlenku miedzi osadzonym na porowatych cząsteczkach glinu. W reaktorze z wielostopniowym złożem fluidalnym gaz i ciała stałe płyną przeciwprądowo. Powstający w reakcji siarczan miedzi jest następnie redukowany metanem.

Zbadano wpływ szybkości przepływu gazu i ciał stałych, czasu przebywania ciał stałych w reaktorze, temperatury oraz stężenia dwutlenku siarki i innych gazów na proces odsiarczania. Wydajność odsiarczania przekraczającą 90% osiągnięto w czterostopniowym reaktorze; stężenie dwutlenku siarki można zredukować z 3000 ppm do mniej niż 300 ppm przy niewielkim zmniejszeniu ciśniena gazu.

ENTSCHWEFELUNG VON GAS DURCH DIE SORPTION VON SCHWEFELDIOXID AUF ALUMINIUM-GASTÜTZTEM KUPFEROXID IM REAKTOR MIT FÜLLKORPER

Entschwefelt werden Vielstoffgemische (Schwefeldioxid, Stickstoffdioxid, Kohlenstoffdioxid und Wasser). Das Entschwefelungsverfahren besteht aus Sorption von Schwefeldioxid auf den porösen Körnern des aluminium-gestützten Kupferoxids. Der Reaktor enthält einen mehrschichtigen Füllkörper. Das Gas und die Festkörper fließen im Gegenstrom. Das während der Reaktion erzeugte Kupfersulfat wird mit Methan reduziert.

Die Untersuchungen umfassen den Einfluß solcher Parameter, wie die Durchflußgeschwindigkeit von Gas und Festkörpern, die Verweilzeit von Festkörpern im Reaktor, Temperatur, Konzentration von Schwefeldioxid und anderen Gasen, auf den Verlauf des Entschwefelungsverfahrens. Der Entschwefelungsgrad beträgt 90 Prozent und wird im vierstufigen Reaktor erzielt. Bei einer geringen Gasdrucksenkung kann die Schwefeldioxidkonzentration von 3000 ppm bis auf $>$ 300 ppm reduziert werden.

ОБЕССЕРИВАНИЕ ГАЗА ПОСРЕДСТВОМ СОРБЦИИ СЕРНИСТОГО ГАЗА НА ОКИСИ МЕДИ, ОСАЖДЁННОЙ НА ЧАСТИЦАХ АЛЮМИНИЯ В РЕАКТОРЕ С ФЛЮИДНЫМ СЛОЕМ

Обсуждено обессеривание воздуха, сернистого газа, двуокиси азота, углекислого газа и водных смесей посредством химической сорбции сернистого газа на окиси меди, осаждённой на пористых частицах алюминия. В реакторе с многоступенчатым флюидным слоем газ и твёрдые тела текут противоточно. Затем образующийся в реакции сульфат меди восстанавливается метаном.

Исследовано влияние скорости прохода газа и твёрдых тел, времени пребывания твёрдых тел в реакторе, температуры, а также концентрации сернистого газа и других газов на процесс обессеривания. Выход обессеривания, превышающий 90%, был достигнут в четырёхступенчатом реакторе; концентрацию сернистого газа можно уменьшить с 3000 млн$^{-1}$ до ниже 300 млн$^{-1}$ при незначительном снижении давления газа.