

## COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

## CONVENTION APPLICATION FOR A PATENT

(1) Here  
Insert (in  
full) Name  
or Names of  
Applicant or  
Applicants,  
followed by  
Address(es).

(1) We ..... METALLGESELLSCHAFT AKTIENGESELLSCHAFT.....  
..... of ..... Reuterweg 14, D-6000 Frankfurt/Main, Federal Republic.....  
..... of Germany.....  
.....  
.....

(2) Here  
Insert Title  
of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2).....  
..... PROCESS OF RECOVERING SULPHUR FROM SULPHIDE MATERIALS WHICH CONTAIN.....  
..... THERMALLY RELEASEABLE SULPHUR.....  
.....

(3) Here Insert  
number(s)  
of basic  
application(s).

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered (3).....  
..... P39.26.723.7.....

(4) Here Insert  
Name of basic  
Country or  
Countries, and  
basic date or  
dates.

for a patent or similar protection made in (4)..... Federal Republic of Germany.....  
..... on 12th August 1989.....  
.....

My address for service is WATERMARK PATENT & TRADEMARK ATTORNEYS  
290 Burwood Road, Hawthorn, Victoria, Australia.

DATED this ..... 9th day of ..... August ..... 1990 .....

(5) Signature(s) of  
Applicant(s)  
or  
Seal of  
Company and  
Signatures of  
its Officers as  
prescribed by  
its Articles of  
Association.

METALLGESELLSCHAFT AKTIENGESELLSCHAFT

(6) .....

..... by .....

..... Stephen K. Plymin .....

..... Registered Patent Attorney .....

To: THE COMMISSIONER OF PATENTS.

## COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

DECLARATION IN SUPPORT OF A CONVENTION  
APPLICATION FOR A PATENT OR PATENT OF ADDITION(1) Here  
insert (in  
full) Name of  
Company.In support of the Convention Application made by<sup>(1)</sup>  
METALLGESELLSCHAFT AKTIENGESELLSCHAFT(2) Here  
insert title  
of Invention.(hereinafter referred to as the applicant) for a Patent  
for an invention entitled:<sup>(2)</sup> PROCESS OF RECOVERING  
SULFUR FROM SULFIDE MATERIALS WHICH CONTAIN THERMALLY RELEASEABLE  
SULFUR(3) Here  
insert full Name  
and Address  
of Company  
official  
authorized  
to make  
declaration.We  <sup>(3)</sup> ANNELIESE GASTEYER and WOLFGANG WAGNER, both  
of.....Reuterweg 14, D-6000 Frankfurt/Main, Federal Republic of Germany

do solemnly and sincerely declare as follows:

(4) Here  
insert basic  
Country or  
Countries  
followed by  
date or dates  
and basic  
Applicant or  
Applicants.1. We are  
.....authorised by the applicant for the patent  
to make this declaration on its behalf.  
2. The basic application as defined by Section 141 of the Act was  
.....made in<sup>(4)</sup> Federal Republic of Germany  
on the ..... 12th .....day of ..... August 1989, by  
METALLGESELLSCHAFT AKTIENGESELLSCHAFT  
XX5XXXXX ..... XX5XXXXX ..... 19XXXXpXXXXX(5) Here  
insert (in  
full) Name  
and Address  
of Actual  
Inventor or  
Inventors.3. <sup>(5)</sup> ARNO FITTING, Heinr.-Heine-Strasse 1, D-6392 Neu-Anspach  
and MARTIN HIRSCH, Ramerstrasse 7, D-6382 Friedrichsdorf, Federal  
Republic of GermanyXis/are the actual inventor s of the invention and the facts upon which the applicant  
is entitled to make the application are as follow:The applicant is the assignee of the invention from the said actual  
inventors4. The basic application referred to in paragraph 2 of this Declaration  
was ..... the first application made in a Convention country in  
respect of the invention the subject of the application.DECLARED at ..... Frankfurt/Main, West Germany  
this. ..... 26th ..... day of ..... 1990.

(6) Signature.

To: THE COMMISSIONER OF PATENTS & AUTHORIZED OFFICERS -  
Anneliese Gasteyer (Anneliese Gasteyer) Wolfgang Wagner (Wolfgang Wagner)



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(12) PATENT ABRIDGMENT (11) Document No. AU-B-60918/90  
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 639474

(54) Title  
PROCESS OF RECOVERING SULPHUR FROM SULPHIDE MATERIALS WHICH CONTAIN THERMALLY RELEASABLE SULPHUR

International Patent Classification(s)  
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(57) Claim

1. A process of recovering elementary sulphur from sulphide materials which contain thermally releasable sulphur, wherein the heat required for the reaction is generated in a fluidised bed by an oxidising roasting of sulphides to form an SO<sub>2</sub>-containing exhaust gas which contains sulphur vapour and is removed from the fluidised bed, the sulphur vapour contained in that exhaust gas is separated and part of the SO<sub>2</sub>-containing gas is recycled as fluidising gas to the fluidised bed, characterised in that the reaction is carried out in a circulating fluidised bed, fresh sulphide material being charged into a top portion of a reactor of the circulating fluidised bed 9, solids concentration in said reactor continuously decreasing from bottom to top, solids are recycled to the reactor in such a manner that the amount of solids recirculated per hour is at least five times the weight of solids contained in the reactor, oxygen-containing gases which contain more than 50% oxygen and SO<sub>2</sub>-containing recirculated gas are charged into a bottom portion of the reactor, the rate of oxygen is so controlled that it is sufficient not only to oxidise the iron content of the sulphide material but also to generate the heat required for the process in that at least 15% of the charged sulphur is oxidised to produce SO<sub>2</sub> and exceeds the amount of SO<sub>2</sub> which can be reduced to elemental sulphur in an intermediate portion of the reactor, a suspension which contains sulphur vapour and SO<sub>2</sub> is withdrawn from the top portion of the reactor and is fed to a recycling cyclone, in which

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substantially all solids are separated, the separated solids are recycled to the intermediate portion of the reactor, sulphur vapour contained in the purified gas is condensed, a major part of the SO<sub>2</sub>-containing gas is recycled to the reactor as recirculated gas, and solids are withdrawn from the bottom portion of the reactor.

639474

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

# COMPLETE SPECIFICATION

(ORIGINAL)

Application Number:  
Lodged:

Class

Int. Class

Complete Specification Lodged:  
Accepted:  
Published:

Priority :

Related Art :

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Complete Specification for the invention entitled:

PROCESS OF RECOVERING SULPHUR FROM SULPHIDE MATERIALS WHICH CONTAIN THERMALLY RELEASEABLE SULPHUR

The following statement is a full description of this invention, including the best method of performing it known to :-

Us

PROCESS OF RECOVERING SULPHUR FROM SULPHIDE MATERIALS  
WHICH CONTAIN THERMALLY RELEASEABLE SULPHUR

DESCRIPTION

5 This invention relates to a process of recovering  
elementary sulphur from sulphide materials which contain  
thermally releasable sulphur, wherein the heat required for  
the reaction is generated in a fluidised bed by an oxidising  
roasting of sulphides to form an SO<sub>2</sub>-containing exhaust gas  
which contains sulphur vapour and is removed from the  
10 fluidised bed, the sulphur vapour contained in that exhaust  
gas is separated and part of the SO<sub>2</sub>-containing gas is  
recycled as fluidising gas to the fluidised bed.

15 Sulphide materials which contain thermally  
releasable sulphur are, e.g., pyrites (FeS<sub>2</sub>) and  
chalcopyrite (CuFeS<sub>2</sub>). Under non-oxidising conditions a  
temperature rise above the dissociation temperature will  
cause the unstable sulphur to be released as a vapour. The  
sulphur is separated from the exhaust gas by condensation.  
Sulphide sulphur may be oxidised in an oxidising atmosphere  
20 to form SO<sub>2</sub> or may be vapourised also as elementary sulphur  
in a reducing atmosphere.

25 German Patent Application M 97 88, Class 12i,21,  
published on September 25, 1952, discloses for the  
production of SO<sub>2</sub> and elementary sulphur from pyrites a  
process in which the pyrites are treated in two spatially  
separated fluidised bed furnaces, which are connected in  
series and contain orthodox fluidised beds. The fresh  
30 pyrites are charged into the first fluidised bed, which is  
supplied from below with a fluidising gas consisting of the  
SO<sub>2</sub>-containing hot gas from the second fluidised bed. The exhaust  
gas from the first fluidised bed contains the  
vapourised elementary sulphur and SO<sub>2</sub>. The solids flow from  
35 the first fluidised bed into the second fluidised bed, which  
is supplied from below with mixed gases consisting of 80%  
SO<sub>2</sub> and 20% O<sub>2</sub>. In the second fluidised bed the partly  
desulphurised pyrites are almost completely roasted with  
formation of SO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. The roasted solids are

withdrawn from the second fluidised bed. The elementary sulphur is separated from the exhaust gas of the first fluidized bed by condensation and by being contacted with sprayed molten sulphur. The  $\text{SO}_2$ -containing gas is recycled in part to the second fluidised bed and another part of said gas is discharged as a product. The two fluidised beds are arranged one in the other in order to improve the heat transfer. In that process the sulphur vapour contained in the first fluidised bed prevents a formation of elementary sulphur from  $\text{SO}_2$ .

German Patent Application M 10,077, Class 12i,17, published on January 8, 1953, discloses a process in which two orthodox fluidised beds are used, which are arranged one over the other, and pyrites and carbon are charged into the upper fluidised bed. The process is carried out as described hereinbefore but in the first bed the carbon acts to reduce all or part of the  $\text{SO}_2$  contained in the fluidising gas to form elementary sulphur. After a condensation of the sulphur the gas which contains  $\text{CO}$ ,  $\text{CO}_2$  and possibly  $\text{SO}_2$  is recycled to the second fluidised bed. In that process too the reduction of  $\text{SO}_2$  in the first fluidised bed is hindered by the sulphur vapour which is present. Besides,  $\text{CS}_2$  and  $\text{COS}$  are formed.

British Patent Specification 731,527 discloses a process in which three orthodox fluidised beds are used, which are arranged one over the other. Iron pyrites and copper pyrites are charged into the first fluidised bed and are fluidised with hot-oxidising gas from the third fluidised bed. Elementary sulphur is recovered by condensation from the exhaust gas from the first fluidised bed. The solids flow through overflow pipes into the second fluidised bed and are treated there under oxidising conditions with the exhaust gas from the first fluidised bed after elementary sulphur has been removed from said exhaust gas and air has been admixed to said exhaust gas. The  $\text{SO}_2$ -containing exhaust gas from the second fluidised bed is fed to an  $\text{SO}_2$ -recovering plant. The solids from the second

fluidised bed flow through downcomers into the third fluidised bed and are reduced there under reducing conditions with producer gas to form  $Fe_3O_4$ . That process does not comprise a formation of elementary sulphur from  $SO_2$  and the supply of producer gas to the first fluidised bed results in the formation of  $CS_2$ ,

5  $COS$ ,  $H_2S$  etc.

It is an object of the invention to expel the thermally releasable sulphur to the largest possible degree, to minimise the sulphur content of the solids which are discharged, to reduce the largest possible amount of  $SO_2$  to elementary sulphur, to minimise the energy consumption in the process and to permit the

10 exhaust gases to be treated in a simple manner.

That object is accomplished in accordance with the invention in that the reaction is carried out in a circulating fluidised bed, fresh sulphide material being charged into a top portion of a reactor of the circulating fluidised bed 9, solids concentration in said reactor continuously decreasing from bottom to top,

15 solids are recycled to the reactor in such a manner that the amount of solids recirculated per hour is at least five times the weight of solids contained in the reactor, oxygen-containing gases which contain more than 50% oxygen and  $SO_2$ -containing recirculated gas are charged into a bottom portion of the reactor,

20 the rate of oxygen is so controlled that it is sufficient not only to oxidise the iron content of the sulphide material but also to generate the heat required for the process in that at least 15% of the charged sulphur is oxidised to produce  $SO_2$  and exceeds the amount of  $SO_2$  which can be reduced to elemental sulphur in

25 an intermediate portion of the reactor, a suspension which contains sulphur vapour and  $SO_2$  is withdrawn from the top portion of the reactor and is fed to a recycling cyclone, in which substantially all solids are separated, the separated solids are recycled to the intermediate portion of the reactor, sulphur vapour contained in the purified gas is condensed, a major part of the  $SO_2$ -containing gas is recycled to the reactor as recirculated gas, and solids are withdrawn from the bottom portion of the reactor. The circulating fluidised bed system consists of

30 the fluidised bed reactor, the recycling cyclone and the return line for the solids which have been separated in the recycling cyclone. The fluidised bed used in accordance with the invention differs from an



"orthodox" fluidised bed, in which a dense phase is separated by a distinct density step from the overlying gas space, in that the fluidised bed reactor contains states of distribution without a defined boundary layer. There is no density step between a dense phase and an overlying gas space but the solids concentration continuously decreases in the reactor from bottom to top.

A definition of the operating conditions by the Froude and Archimedes numbers results in the following ranges:

$$0.1 \leq \frac{3/4 \times Fr^2 \times \frac{\rho_g}{\rho_k - \rho_g}}{10}$$

or  $0.01 \leq Ar \leq 100$

wherein

$$Ar = \frac{d_k^3 \times g(\rho_k - \rho_g)}{\rho_g \times v^2} \quad \text{and}$$

$$Fr^2 = \frac{u^2}{g \times d_k}$$

and

$u$  = the relative gas velocity in m/sec.

$Ar$  = the Archimedes number

$Fr$  = the Froude number

$\rho_g$  = the density of the gas in  $\text{kg/m}^3$

$\rho_k$  = the density of the solid particle in  $\text{kg/m}^3$

$d_k$  = the diameter of the spherical particle in m

$v$  = the kinematic viscosity in  $\text{m}^2/\text{sec.}$

$g$  = the acceleration due to gravity in  $\text{m/sec.}^2$

The solids which have been entrained by the gases leaving the fluidised bed reactor are recycled to the fluidised bed reactor in such a manner that the amount of solids recirculated per hour is at least 5 times the weight of the solids contained in the fluidised bed reactor. The oxygen-containing gases which are introduced as a fluidising gas into the bottom portion of the fluidised bed reactor

contain more than 50% oxygen. The rate at which oxygen is introduced is controlled to be sufficient to oxidise the iron content to  $Fe_3O_4$  and to oxidise part of the sulphide sulphur to  $SO_2$  in the bottom portion of the fluidised bed reactor. The proportion of the sulphide sulphur which is oxidised to  $SO_2$  must be at least so large that the heat generated by the oxidation is sufficient to meet the demand of the system. In the intermediate portion of the fluidised bed reactor, sulphide iron is reacted with  $SO_2$  to  $Fe_3O_4$  and elementary sulphur vapour. The amount of  $SO_2$  produced in the bottom portion to meet the heat demand is at least 15% of the sulphur content which has been supplied and exceeds the amount of  $SO_2$  which can be reduced to elementary sulphur in the intermediate portion. For this reason a corresponding amount of  $SO_2$  must be removed after sulphur has been condensed out of the gas stream. If  $SO_2$  is to be removed at a relatively high rate, the rate at which oxygen is supplied to the bottom portion of the fluidised bed reactor will be increased accordingly and the heat, which will then be generated at a higher rate, will be dissipated. The thermally releasable sulphur will be released in the top portion of the fluidised bed reactor. The solids which have been separated in the recycling cyclone are recycled to the intermediate portion of the reactor above the level which is spaced from the bottom end of the reactor by 40% of the height of the reactor. If the sulphide material which is fed contains non-ferrous metals in addition to iron the above remarks will be analogously applicable also to the non-ferrous metal content. The circulated fluidised bed system may optionally be operated under a superatmospheric pressure.

In accordance with a preferred feature the sulphide material is preheated by a suspension-type heat exchanger with the gases leaving the recycling cyclone and is then charged into the top portion of the reactor. The preheating may optionally be effected in a plurality of stages in a plurality of suspension-type heat exchangers. In that case part of the heat content of the exhaust gas from the recycling cyclone can be utilised to meet the heat demand.

In accordance with a preferred feature, the rate at which  $\text{SO}_2$  is recycled in the recirculated gas is at 5 times and preferably 7 to 15 times the rate which is stoichiometrically required for the reaction  $3 \text{FeS} + \text{SO}_2 = \text{Fe}_3\text{O}_4 + 5 \text{S}$ . The recirculation of  $\text{SO}_2$  at that rate will result in a good adaptation of the reaction rates of the oxidation of sulphide sulphur in the bottom portion of the reactor and the reaction of  $\text{SO}_2$  with sulphide sulphur to form elementary sulphur in the intermediate portion of the reactor so that elementary sulphur will substantially be produced from the  $\text{SO}_2$  which has been formed.

In accordance with a preferred feature the recirculated gas is preheated by an indirect heat exchange before said gas is fed to the reactor. Preheating is preferably effected to a temperature of 600 to 800°C. As a result of that preheating the energy balance of the process is improved and less sulphide sulphur must be oxidised to  $\text{SO}_2$ .

In accordance with a preferred feature the preheating is effected in an orthodox fluidised bed with the solids which have been discharged from the reader of the circulating fluidised bed system, oxygen-containing gas is used as a fluidising gas, the heated-up fluidising gas is fed as secondary gas through the shell of the reactor into the bottom portion of the reactor, and the preheated recirculated gas is fed to the bottom portion of the reactor. The recirculated gas is preheated by an indirect heat exchange in the orthodox fluidised bed. Because the oxygen-containing fluidising gas which has been heated up contains dust, it will not produce an adverse effect on the bottom of the reactor because said gas is supplied as a secondary gas. An after reaction will take place in the orthodox fluidised bed so that a small residual content of sulphur will also be oxidised.

The invention will be explained more in detail with reference to a flow scheme.

The sulphide material which contains thermally releasable sulphur is supplied through line 1 to the suspension-type heat exchanger 2 and is then fed through line 3 to a gas-purifying electrostatic precipitator 4, with which a preliminary separator is associated and in which the sulphide material is separated from the gas stream, which is then fed through line 5 to the top portion of the fluidised bed reactor 6. A suspension consisting of solids and gases is fed from the fluidised bed reactor 6 through line 7 to the separating cyclone 8. The separated solids are recycled through the recycle line 9 to the bottom portion of the fluidised bed reactor 6. The gases flow from the recycling cyclone 8 to the suspension-type heat exchanger 2. The gases which have been separated in the gas-purifying electrostatic precipitator 4 are fed through line 10 to the sulphur condenser 11, in which they are indirectly cooled below the condensation temperature of sulphur. Liquid sulphur is fed through line 12 to a tank 13. The gas is fed through line 14 to a sulphur scrubber 15 and is washed there with liquid sulphur, which is recirculated through a pump 16, a line 17 and a line 18. The sulphur product is withdrawn from the tank 13 through line 19. The SO<sub>2</sub>-containing exhaust gas from which the sulphur had been removed is withdrawn from the sulphur scrubber 15 in line 20 by the fan 21. A partial stream of said exhaust gas is fed through line 22 to the plant 23 and is used therein to produce sulphuric acid, which is withdrawn through line 24. Oxygen is supplied through line 25 to the remaining part of the exhaust gas. A partial stream of the mixed gases is fed through line 26 to the fluidised bed cooler 27 and is heated up there by an indirect heat exchange and is supplied through line 28 as a fluidising gas to the bottom portion of the fluidised bed reactor 6. The other partial stream of the mixed gases is fed through line 29 as a fluidising gas to the fluidised bed cooler 27 and is heated up there by a direct heat exchange and is then supplied through line 30 to

the cyclone separator 31, where most of the entrained solids are removed from the gas, which is then fed through line 32 as a secondary gas to the bottom portion of the fluidised bed reactor 6. The solids which have been separated in the cyclone separator 31 are recycled through line 33 to the fluidised bed cooler 27. The solids which have been withdrawn from the fluidised bed reactor 6 are fed through line 34 to the fluidised bed cooler 27 and are cooled there and then discharged through line 35.

The scheme indicated by dotted lines illustrates a mode of operation in which a fluidised bed cooler is not employed. In that case the recirculated exhaust gas is fed through line 36 to a heat exchanger 37 and is heated up there by an indirect heat exchange with hot gases. The hot gases are produced by a combustion of air 38 and fuel 39 and are carried off through line 40. The gas which has been heated up is then fed as a fluidising gas through line 28 to the fluidised bed reactor 6. The solids which have been discharged from the fluidised bed reactor 6 are fed through line 34a to a watercooled screw conveyor 41 and are cooled there and discharged through line 35a. Water is supplied to the watercooled screw conveyor through line 42 and is withdrawn through line 43.

EXAMPLES

The starting material employed contained 23.3% Fe, 21.8% S, 31.4%  $\text{SiO}_2$ , 8.0%  $\text{Al}_2\text{O}_3$  and 2.9% CaO. 80% of the sulphur content were present as  $\text{FeS}_2$  and 20% as FeS. The particle size was less than 0.5 mm. The fluidised bed reactor was 1.1 m in diameter and had a height of 15 m.

EXAMPLE 1

The mode of operation was shown in the drawing with use of a fluidised bed cooler. Fresh material at a rate of 6040 kg/h was supplied to the suspension-type heat exchanger. The suspension was fed to the gas-purifying electrostatic precipitator at a temperature 550°C. The gas leaving the gas-purifying electrostatic precipitator contained  $\text{SO}_2$  at a rate of 2719  $\text{sm}^3/\text{h}$  ( $\text{sm}^3$  = standard cubic



metre) and  $333 \text{ sm}^3/\text{h}$   $\text{S}_2$  and was cooled to  $130^\circ\text{C}$  in the sulphur condenser. Elementary sulphur was produced at a rate of  $950 \text{ kg/h}$ . The partial stream fed to the plant for producing sulphuric acid contained  $\text{SO}_2$  at a rate of  $219 \text{ sm}^3/\text{h}$  and the partial stream which was recirculated contained  $\text{SO}_2$  at a rate of  $2500 \text{ sm}^3/\text{h}$ .  $\text{O}_2$  at a rate of  $576 \text{ sm}^3/\text{h}$  was added to the latter partial stream. A partial stream at a rate of  $1200 \text{ sm}^3/\text{h}$  of the mixed gases was heated up to  $500^\circ\text{C}$  in a fluidised bed cooler and was then fed as a fluidising gas to the bottom portion of the fluidised bed reactor. The remaining partial stream at a rate of  $1876 \text{ sm}^3/\text{h}$  was fed as fluidising gas to the fluidised bed cooler and at a temperature of  $800^\circ\text{C}$  as secondary gas to the fluidised bed reactor. The solids which were withdrawn from the bottom portion of the fluidised bed reactor contained 2% S. Solids which contained 1% S were withdrawn from the fluidised bed cooler at a rate of  $5050 \text{ kg/h}$ . The temperature in the fluidised bed reactor amounted to  $1000^\circ\text{C}$ .

EXAMPLE 2

The process was carried out with the plant having no fluidised bed cooler as shown in the drawing. Fresh material was supplied to the suspension-type heat exchanger at a rate of  $6040 \text{ kg/h}$ . The suspension was fed to the gas-purifying electrostatic precipitator at a temperature of  $550^\circ\text{C}$ . The gas leaving the gas-purifying electrostatic precipitator contained  $\text{SO}_2$  at a rate of  $2684 \text{ sm}^3/\text{h}$  and  $\text{S}_2$  at a rate of  $350 \text{ sm}^3/\text{h}$ .

$\text{O}_2$  at a rate of  $541 \text{ sm}^3/\text{h}$  was added to that partial stream. In the heat exchanger the mixed gases were heated up to  $700^\circ\text{C}$  in that heat at a rate of  $0.9 \text{ Gcal/h}$  was supplied by an indirect heat exchange. The mixed gases were subsequently fed as fluidising gas to the fluidised bed reactor. The temperature in the fluidised bed reactor amounted to  $1000^\circ\text{C}$ . Solids having a sulphur content of 1% were withdrawn from the water-cooled screw-conveyor at a rate of  $5070 \text{ kg/h}$ .

The advantages afforded by the invention reside in that a backmixing of gases in the fluidised bed reactor is virtually prevented by the upwardly rising plug flow in the fluidised bed reactor so that three zones can be adjusted in the reactor and the different reactions can separately be carried out in said three zones. Iron and sulphide sulphur are rapidly oxidised in the oxidising bottom zone so that the oxygen is virtually completely consumed in that zone and cannot influence the reduction of  $\text{SO}_2$  to elementary sulphur in the reducing intermediate zone. As the sulphur is thermally released in the top zone, the reduction in the intermediate zone is not influenced also by the elementary sulphur which has been vapourised. As a result, a large part of the sulphur content which has been supplied can be recovered as elementary sulphur and  $\text{SO}_2$  must be removed from circulation only at a low rate. On the other hand the system is highly flexible as regards the desired ration of the rates at which elementary sulphur and  $\text{SO}_2$  are produced if  $\text{SO}_2$  is to be discharged at a higher rate.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process of recovering elementary sulphur from sulphide materials which contain thermally releasable sulphur, wherein the heat required for the reaction is generated in a fluidised bed by an oxidising roasting of sulphides to form an SO<sub>2</sub>-containing exhaust gas which contains sulphur vapour and is removed from the fluidised bed, the sulphur vapour contained in that exhaust gas is separated and part of the SO<sub>2</sub>-containing gas is recycled as fluidising gas to the fluidised bed, characterised in that the reaction is carried out in a circulating fluidised bed, fresh sulphide material being charged into a top portion of a reactor of the circulating fluidised bed 9, solids concentration in said reactor continuously decreasing from bottom to top, solids are recycled to the reactor in such a manner that the amount of solids recirculated per hour is at least five times the weight of solids contained in the reactor, oxygen-containing gases which contain more than 50% oxygen and SO<sub>2</sub>-containing recirculated gas are charged into a bottom portion of the reactor, the rate of oxygen is so controlled that it is sufficient not only to oxidise the iron content of the sulphide material but also to generate the heat required for the process in that at least 15% of the charged sulphur is oxidised to produce SO<sub>2</sub> and exceeds the amount of SO<sub>2</sub> which can be reduced to elemental sulphur in an intermediate portion of the reactor, a suspension which contains sulphur vapour and SO<sub>2</sub> is withdrawn from the top portion of the reactor and is fed to a recycling cyclone, in which substantially all solids are separated, the separated solids are recycled to the intermediate portion of the reactor, sulphur vapour contained in the purified gas is condensed, a major part of the SO<sub>2</sub>-containing gas is recycled to the reactor as recirculated gas, and solids are withdrawn from the bottom portion of the reactor.
2. A process according to claim 1, characterised in that the sulphide material is preheated by a suspension-type heat exchanger with the gases leaving the recycling cyclone and is then charged into the top portion of the reactor.
3. A process according to claim 1 or 2, characterised in that the rate at which SO<sub>2</sub> is recycled in the recirculated gas is at least five times and preferably



12a

seven to fifteen times the rate which is stoichiometrically required for the reaction  
 $3\text{FeS} + 2\text{SO}_2 = \text{Fe}_3\text{O}_4 + 5\text{S}$ .

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4. A process according to any one of claims 1 to 3, characterised in that the recirculated gas is preheated by an indirect heat exchange before said gas is fed to the reactor.

5. A process according to claim 4, characterised in that the preheating is effected in an orthodox fluidised bed with the solids which have been discharged from the reactor of the circulating fluidised bed system, oxygen-containing gas is used as a fluidising gas, the heated-up fluidising gas is fed as secondary gas through the shell of the reactor into the bottom portion of the reactor, and the preheated recirculated gas is fed to the bottom portion of the reactor.

6. A process of recovering elemental sulphur from sulphide materials which contain thermally releasable sulphur, substantially as hereinbefore described with reference to the accompanying drawings.

7. A process of recovering elemental sulphur from sulphide materials which contain thermally releasable sulphur, substantially as hereinbefore described with reference to the Examples.

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