

Description

The invention relates to agents for purifying gases and waste gases from acids and heavy metals, a process for manufacturing these agents and a process for purifying gases and waste gases from heavy metals and acids.

During thermal processes, e.g. metallurgical processes, coal firings and waste incinerations, waste gases are produced which are polluted with volatile heavy metals, e.g. cadmium, mercury, thallium, arsenic, antimony and lead. Elementary heavy metals or salts, in particular chlorides and oxides, are involved here.

Usually the gases are cooled and the heavy metals washed out in the wet state. This is often not sufficient if the heavy metals are present in elementary form. Mercury, for example, is often emitted as an element. It cannot then be separated from the gas, even by means of wet cleaning. There is the added problem that, even after the wet cleaning, volatile heavy metals are emitted as aerosols and/or fine dust that is difficult to separate.

A further process of prior art works with suspensions of sulphur or sulphur compounds or with aqueous solutions of thio compounds, e.g. thio urea. The solutions or suspensions are sprayed through a nozzle into the gas flow and the compounds formed from mercury and sulphur are separated on electrostatic filters.

The mercury separation rate of 70% is however too low to ensure compliance with the limit value of 0.2 mg/m^3 . The inadequate Hg separation rate may be attributable inter alia to the addition of water to the gas flow and to the considerable content of strong acids in the gas flow if waste gases from waste incineration plants are treated.

In addition a number of processes are also known in which a dry separation of mercury from waste gases takes place.

One method consists in passing waste gas flows through activated carbon filters. Although this leads to a reduction in the content of volatile heavy metals, e.g. mercury, this process is nevertheless burdened with considerable costs and dangers, since large amounts of highly activated carbon have to be used and there is always the danger of smouldering fires in the coal bed. In addition, heavy-metal-containing dust, which is difficult to separate, is emitted via the fines always present.

There has therefore been no lack of attempts to convert the volatile heavy metals with sulphur or sulphides into sulphides that are not easily volatilized and to separate them from the gas flow.

A known method consists in applying sulphur to activated carbon and passing the gas flow over the latter. Although the mercury separation is quite effective, the problems of spontaneous ignition and the emission of fines still exist.

It has also already been proposed that sulphur or water-insoluble sulphur compounds, e.g. ZnS , be sprayed through a nozzle together with Ca(OH)_2 powder into the waste gas flow from waste incineration plants and that mercury be thus separated. Although 1 g/m^3 of ZnS was used at 200 to 250°C , the Hg separation rate of 60% was too low to ensure an Hg limit value of 0.2 mg/m^3 .

From DE-A-37 02 306 there is known a process for separating heavy metals from furnace waste gases, in which heavy-metal-bonding substances are added to the waste gas and the heavy metal compounds formed that are not easily volatilized are separated on dust separation devices. The compound 3-mercapto-S-triazine mentioned in this printed publication as an example of a heavy-metal-bonding substance does not however decompose in the waste gas in such a way that elementary sulphur is obtained in the reaction chamber.

EP-A-0 292 083 describes a process for manufacturing reactive calcium hydroxides for gas and waste gas purification, in which the calcium hydroxide is brought into contact inter alia with mercury-bonding substances such as hydrogen sulphide, sodium hydrogen sulphide, sodium sulphide or 3-mercapto-S-triazine. These named sulphur-containing compounds also do not decompose with the formation of elementary sulphur.

In WO 88/09203 surface-active substances mixed with calcium hydroxide are described, where the surface-active substances are still able to contain pollutant-bonding substances such as sodium sulphide, mercaptans or 3-mercapto-S-triazine. The sulphur-containing compounds specified are not however capable of giving off elementary sulphur in the waste gas.

From DE-A-29 48 305 there is known a process for the dry cleaning of mercury-containing gases and waste gases from thermal processes, in which the gases are treated with metals and/or alloys which form amalgams with the mercury.

There can be introduced additionally into the waste gas flow, together with the amalgam-forming metals or alloys, further basic substances for binding acid pollutants.

DE-A-23 30 854 relates to the removal of mercury vapours from the gaseous phase by means of a water-insoluble metal sulphide, which is applied to a silicic acid and/or alumina support, is water-soluble and reacts with mercury.

In FR-A-2 529 802 an absorption mass for removing mercury from a gas is described. There are named as suitable absorption masses inorganic compounds such as aluminium oxide, silicon oxide and cement.

From DE-A-27 28 692 there is known a method for removing mercury-containing impurities from gases. The removal takes place by passing the gases through a filter bed comprising an absorber which is formed by a support and one or more absorption agents consisting of natural sulphide minerals, synthetic metal sulphides and/or sulphur.

The process described in US-A-4 101 631 relates to the selective adsorption of mercury from gas flows by means of elementary sulphur precipitated on molecular sieves.

In US-A-4 206 183 a process for removing mercury-containing impurities from gases is described. In this process agents are used in which sulphides or sulphur have been deposited on supports such as pumice. The mercury contained in the gas is converted into insoluble mercury.

* DE-A-34 39 059 finally relates to an absorption agent for the dry removal of sulphur dioxide from flue gases. In order to enhance the efficiency of the separation of sulphur dioxide, manganese carbonate or manganese oxide are added to fine-grained, inorganic alkaline-earth compounds.

All of the above-mentioned agents and processes exhibit the disadvantage that the reliable separation of mercury from waste gas flows is not possible with them.

The present invention is therefore based on the problem of separating as quantitatively as possible from gas flows, mainly from waste incineration plants, volatile heavy metals, in particular mercury, in their various compound forms and also in elementary form, selectively and without cooling operations. It is intended in addition to specify a simple and inexpensive process for the combined separation of volatile

heavy metals and acid components from gas flows. At the same time the reduction of the heavy metal content in the waste gas flow must be sufficiently great that the existing limit values, e.g. for Hg, Cd, Ti and As, may be reliably adhered to.

The invention solves this problem by means of an agent for purifying gases and waste gases from acids and heavy metals according to the independent claim 1. Preferred developments of the agent are described in claims 2 to 10.

The invention also creates a process for manufacturing dry or water-containing powders based on calcium hydroxide and sulphur-containing, heavy-metal-forming substances or sulphur-containing heavy-metal-bonding substances and surface-active substances for gas and waste gas purification according to independent claim 11. A preferred development of this process is described in independent claim 12.

According to a further aspect of the invention, processes for purifying gases and waste gases from heavy metals and acids are specified according to the independent claims 13 and 17. Preferred developments of the process according to claim 13 are described in the independent claims 14 to 16.

According to the invention the solution of one aspect of the problem posed takes place in two stages, where in a 1st stage calcium hydroxides are manufactured that contain water-soluble, sulphur-containing substances that react with the acids present in the waste gas to give off sulphur, which in a 2nd stage are caused to act in a dry or quasi-dry process on the volatile, i.e. vaporous, heavy metals of the waste gas and are separated again out of the waste gas flow.

• A major advantage of the water-soluble, sulphur-containing substances which react with the acids present in the waste gas to give off sulphur consists in the fact that they can be applied to the calcium hydroxide either dissolved in water during the slaking process or extremely finely distributed after the slaking. The application to surface-active substances is also greatly facilitated. The extremely fine distribution favours the reactions with the heavy metals considerably.

• In addition to this, water films form on calcium hydroxide and on the surface-active substances, which dissolve the sulphur-containing substances proportionately. Heavy metals, which are volatile as salts, dissolve in the water film and react rapidly with the sulphur given off by the water-soluble, sulphur-containing compounds.

The separation of the volatile heavy metals is greatly facilitated by these mechanisms.

According to the invention use is made in particular of thiosulphates and polysulphides as water-soluble, sulphur-containing substances which give off sulphur under the action of acid. Particularly preferred are alkali and alkaline-earth compounds of the thiosulphates and polysulphides.

The sulphur released from the above-mentioned substances is formed in extremely finely distributed form and is highly suitable for the bonding of volatile heavy metals of the most varied types. Since the waste gas flows from waste incineration plants and also from other incineration systems always contain acids, the release of sulphur from the substances is ensured.

Also suitable as a group of substances giving off sulphur under acid reaction conditions are the polysulphides with the general formula M_2S_n , where n can assume the values 2, 3, 4, 5 and higher and M symbolizes metals. These polysulphides deposit sulphur under the action of acids, which together with the hydrogen sulphide likewise released acts in a highly active form on the volatile heavy metals.

Also usable as compounds giving off sulphur are the salts of polythionic acids. The salts of polythionic acids decompose under the action of acids into sulphur, sulphurous acid and sulphuric acid. The sulphur liberated is likewise extremely suitable for the bonding of volatile heavy metals in gas and waste gas flows.

A preferred embodiment of the process according to the invention for purifying gases and waste gases from volatile heavy metals now consists in water-soluble, sulphur-containing substances which react with the acids present in the waste gas to give off sulphur either being applied, together with calcium hydroxide, to calcium hydroxide or being used mixed with calcium hydroxide.

The manufacture according to the invention of dry or water-containing powders based on calcium hydroxide for purifying gases and waste gases from heavy metals takes place by water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur, or surface-active substances and water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur, being added to the unhydrated lime before slaking the

unhydrated lime and/or to the slaking water during the slaking and/or to the calcium hydroxide after the slaking.

The combining of water-soluble, sulphur-containing compounds with calcium hydroxide takes place preferably by the sulphur-containing compounds being added to the water required for the slaking.

One embodiment consists e.g. in thiosulphates being dissolved in the slaking water and this solution being used for slaking unhydrated lime. The thiosulphate is thereby distributed in extremely fine form and uniformly over the calcium hydroxide and is therefore available in a particularly reactive form for further conversion.

In this case the slaking process can be carried out so that partial slaking takes place first of all with pure water and then the complete slaking with water that contains the water-soluble, sulphur-containing substances that react with the acids present in the waste gas to give off sulphur.

It is also possible, however, to apply the above-mentioned sulphur-containing compounds to calcium hydroxide either in solid form as an extremely fine powder or else in dissolved, concentrated form.

If a subsequent application to calcium hydroxide via solutions takes place, a calcium hydroxide powder is obtained which may contain up to 3% by wt, occasionally up to 5% by wt, of water.

Another possible way of combining the water-soluble, sulphur-containing compounds which give off sulphur under the action of the acids present in the waste gas with calcium hydroxide consists in these compounds being added to the unhydrated lime and the unhydrated lime then being slaked. In all these cases the water-soluble, sulphur-containing compounds are present in extremely fine form distributed in calcium hydroxide. A major advantage of this method of manufacture consists in the fact that unhydrated lime and the water-soluble, sulphur-containing compounds are pre-mixed intensively, e.g. in the lime works, and the mixture is not slaked until it reaches the user. The possession of additional equipment by the user is therefore unnecessary.

These methods of manufacture can be controlled in such a way that the agents mentioned and specified more precisely in claims 1 to 10 are obtained on the basis of calcium hydroxide.

Particularly favourable use can be made of agents which exhibit a content of water-soluble, sulphur-containing substances that react with the acids present in the waste gas to give off sulphur in the range from 0.01 to 5% by wt, preferably 0.1 to 1% by wt, in particular 0.2 to 0.6% by wt.

Depending on the degree of pollution of the waste gases containing volatile heavy metals, use can be made of highly-doped calcium hydroxides or amounts, varying after adjustment in continuous operation, of calcium hydroxide-based agents with different degrees of doping.

In addition there can be manufactured and used according to the invention agents which contain, in addition to the contents in water-soluble, sulphur-containing substances which react with the acids present in the waste gas to give off sulphur, also 0.5 to 10% by wt of surface-active substances.

Possible surface-active substances are in particular activated carbon, lignite-open-hearth coke, silica gel, diatomaceous earth and/or activated aluminium oxide.

The water-soluble, sulphur-containing substances which react with the acids present in the waste gas to give off sulphur can be applied to the surface-active substances via aqueous solutions or be mixed mechanically with them.

The application to the surface-active substances ideally takes place in an independent handling stage, but it can also be accomplished with great success during the slaking process.

This can be carried out by the water-soluble, sulphur-containing substances and the surface-active substances being mixed with unhydrated lime and said unhydrated lime then being slaked. It is also possible, however, to mix unhydrated lime with the surface-active substances and then to slake it with water that contains the water-soluble, sulphur-containing substances.

In this way, for example, water-soluble polysulphides, thiosulphates and polythionic acids can be successfully applied to lignite-open-hearth coke and manufactured in dry form by evaporation of the water.

Surface-active substances are highly suitable for the separation of volatile heavy metals. They are in most cases already capable of bonding heavy metals on their own, but this effect is further increased considerably by the presence of water-

soluble, sulphur-containing substances which react with the acids present in the waste gas to give off sulphur.

Another form of the combining of surface-active substances and water-soluble, sulphur-containing substances which react with the acids present in the waste gas to give off sulphur consists in the latter being combined with the solid surface-active substances in extremely finely distributed form by grinding or else blending.

An embodiment of the process according to the invention for purifying acid-containing gases and waste gases consists in the gas or waste gas flows being treated with the specified agents in the temperature range from 0 to 400°C, preferably 20 to 300°C, in particular 80 to 250° C.

At temperatures above 400°C there is the danger of the rapid combustion of the sulphur-containing compounds. The main area of application lies in the temperature range from 20 to approx. 300°C. At 200 to 250°C most of the waste gases from incineration plants pass after the boiler into the purification units. It therefore makes particular sense to separate the volatile heavy metals out of the hot waste gases at 200 to 250°C. The thiosulphates, the polysulphides and the salts of polythionic acids are particularly suitable for this. The thiosulphates are quite particularly suitable, since they are temperature-stable and are able to react rapidly with the volatile heavy metals at high temperatures.

The ratio of the sulphur compounds used according to the invention to the heavy metals to be separated is characterised by the fact that the heavy metals present in extremely small amounts can be treated with a substantial excess of sulphur-containing compounds without particular economic costs.

According to the invention it is advisable to use the sulphur-containing substances which react with the acids present in the waste gas to give off sulphur, in particular sodium thiosulphate, in a quantity of from 1 to 1000, preferably a quantity of from 25 to 500, in relation to mercury. "In a quantity" means that for one unit by weight of mercury the same unit by weight of sulphur-containing sulphur is used for a quantity of 1.

The preferred range of application is a quantity of from 25 to 500. With a stoichiometry of this kind the volatile heavy metals can be reliably separated without the process becoming uneconomic.

The advantage of compounds giving off sulphur, such as thiosulphates, lies in the fact that the sulphur occurs in extremely finely distributed form during the decomposition under the action of acids.

The main advantage of the process according to the invention can be considered to lie in the fact that the water-soluble, sulphur-containing substances used for bonding the volatile heavy metals of the waste gases, which react with the acids present in the waste gas to give off sulphur, can be introduced into the gas flow with considerable amounts of Ca(OH)_2 powder as carrier. This ensures a reliable distribution of the sulphur-containing substances in the gas flow. In addition, if a fabric filter is used, a reaction layer is present which the waste gas to be purified has to pass through.

Ca(OH)_2 has consequently not only the function of an acid binder, but also the function of creating reaction surfaces and reaction possibilities for the sulphur-containing substances.

In addition, Ca(OH)_2 has the function of absorbing and thereby neutralizing oxidation products, e.g. SO_2 or SO_3 , obtained from the sulphur formed or from the sulphur-containing substances. A high excess of sulphur-containing substances relative to the volatile heavy metals can therefore be used, since no emissions of SO_2 or SO_3 can be expected. Up to 100% separation of the volatile heavy metals is achievable.

Even at the high reaction temperatures of 200°C the volatile heavy metals are separated with separation rates of more than 70%.

The reaction products formed from the sulphur compounds and the volatile heavy metals can be separated on conventional filters, preferably fabric filters or electrostatic filters, in cyclones or else by wet cleaning.

The process is suitable for the treatment of gases and waste gases from production processes, e.g. metallurgical processes, chlor-alkali electrolysis, blast-furnace processes, and of waste gases from power plants, waste incineration and special waste incineration plants, plants of the glass and ceramics industry, furnaces, aluminium smelting works and incineration plants.

It can be used for dry sorption and dry sorption with water conditioning.

The invention will be explained below by means of an example:

Example:

111 mg of sodium thiosulphate were dissolved in 17 ml of water. 28 g of unhydrated lime were slaked with the latter. The dry calcium hydroxide obtained was used for purifying waste gas.

10.5 l of a waste gas with the following composition were passed through 265 mg of this product at 192°C:

- nitrogen	80% by vol.
- oxygen	20% by vol.
- humidity	289 mg/l
- HCl	12.1 mg/l
- HgCl	0.7 µg/l

5.7 µg out of a total of 7.4 µg HgCl were separated. This amounts to a separation rate of 76.8%.



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Claims

1. An agent for purifying gases and waste gases from acids and heavy metals, **characterized in that** it consists of a dry powder based on reactive calcium hydroxide and water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur.
2. An agent according to Claim 1, **characterized in that** the calcium hydroxide has a content of from 0.01 to 5% by weight, preferably 0.1 to 1% by weight, in particular 0.2 to 0.6% by weight of water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur.
3. An agent according to Claim 1 or 2, **characterized** by a grain size of $< 200 \mu\text{m}$.
4. An agent according to one of the preceding Claims, **characterized in that** the dry powder based on reactive calcium hydroxide additionally contains surface-active substances.
5. An agent according to Claim 4, **characterized in that** the calcium hydroxide contains from 0.5 to 10% by weight of surface-active substances.
6. An agent according to Claim 4 or 5, **characterized in that** the water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur are applied to the surface-active substances.
7. An agent according to Claim 4 or 5, **characterized in that** the water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur are mixed with the surface-active substances.



8. An agent according to one of the preceding Claims, **characterized in that** the water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur are selected from the group of polysulphides, polythionates and thiosulphates, in particular in the form of alkaline and alkaline-earth compounds.
9. An agent according to one of the preceding Claims, **characterized by** a water content of from 1 to 5% (by weight), preferably from 0.5 to 3% by weight.
10. An agent according to one of Claims 4 to 9, **characterized in that** the surface-active substances are selected from the group of activated carbon, lignite-open-hearth coke, activated aluminium oxide, silica gel and/or diatomaceous earth.
11. A process for preparing dry or water-containing powders based on calcium hydroxide and sulphur-containing heavy-metal-bonding substances or sulphur-containing heavy-metal-bonding substances and surface-active substances for purifying gases and waste gases from heavy metals and acids according to one of the preceding Claims, **characterized in that** water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur, or surface-active substances and water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur are added to the unhydrated lime before slaking the unhydrated lime and/or to the slaking water during the slaking and/or to the calcium hydroxide after the slaking.
12. A process according to Claim 11, **characterized in that** the water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur are applied, dissolved in water, to calcium hydroxide.
13. A process for purifying gases and waste gases from heavy metals and acids with calcium hydroxide and sulphur-containing substances or calcium



hydroxide, sulphur-containing substances and surface-active substances, **characterized in that** finely powdered, dry calcium hydroxide or finely powdered calcium hydroxide with a water content of from 0.1 to 5% by weight, preferably from 0.5 to 3% by weight, with a content of water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur, or calcium hydroxide with surface-active substances onto which water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur are applied are added to the gas or waste-gas flow, and the sulphidized heavy metals and the reaction products from acids and $\text{Ca}(\text{OH})_2$ from the gas or waste-gas flows are precipitated on suitable separation devices, preferably on fabric filters.

14. A process according to Claim 13, **characterized in that** the agents claimed in Claims 1 to 10 are introduced.
15. A process according to one of Claims 13 and 14, **characterized in that** the gas or waste-gas flows are treated with sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur, in the temperature range of from 0° to 400°C , preferably from 20° to 300°C , in particular from 80° to 250°C .
16. A process according to one of Claims 13 to 15, **characterized in that** the sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur, in particular sodium thiosulphate, are introduced in a ratio to the volatile heavy metals, preferably mercury, in a quantity of from 1 to 1000, preferably in a quantity of from 25 to 500.
17. A process for purifying acid-containing gases and waste gases from the volatile heavy metals contained therein, **characterized in that** the water-soluble, sulphur-containing substances reacting with the acids present in the waste gas to give off sulphur, are introduced in the temperature ranges according to Claim 15 and with the stoichiometric ratio according to Claims 16 [*sic*].