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**Method for total material, emission-free utilisation by high-temperature recycling and by fractional material- specific' conversion of the resultant synthesis raw gas**

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## Abstract

The invention relates to a method and the devices for emission-free total material utilisation of all the ingredients of community or industrial wastes of all types by gasification at high temperatures and processing of the resulting synthesis raw gas, whereby by fractional conversion of all the main ingredients such as hydrogen, carbon monoxide and carbon dioxide, and also the ingredients water, heavy metals, sulphur, chlorine and sodium may be supplied for reuse as a raw material.

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**COMPLETE SPECIFICATION**

**STANDARD PATENT**

**Applicant(s):**

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**Invention Title:**

METHOD FOR TOTAL MATERIAL, EMISSION-FREE UTILISATION BY HIGH-TEMPERATURE RECYCLING AND BY FRACTIONAL MATERIAL-SPECIFIC CONVERSION OF THE RESULTANT SYNTHESIS RAW GAS

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

# Method for Total Material, Emission-free Utilisation by High-temperature Recycling and by Fractional Material-specific Conversion of the Resultant Synthesis Raw Gas

The invention relates to a method of recovery of usable materials, or rendering them useful, from synthesis raw gas, which occurs during the gasification of community or other wastes, preferably also for toxic and special waste of any type, according to the preamble to claim 1, and to a device for carrying out the method.

Gasification of waste is becoming increasingly important as a method for thermal waste treatment, above all because of its great potential for destroying toxins. In addition, the synthesis gas is obtained as a thermally or chemically usable material, and also Fe metals and vitrified minerals, occur in a directly usable form. However, the synthesis raw gas also still contains heavy metals, chlorine and sulphur. These elements - in themselves useful as chemical base materials - are for the biosphere either environmental toxins (heavy metals), or their reaction products, above all with moisture, are ingredients of acid rain. Gas washing of the synthesis raw gas is therefore essential and has for a long time been part of prior art in many different embodiments. Filters (textile), adsorption (activated carbon, precipitation reactions and ion-exchange) are generally used for cleaning, i.e. also for synthesis gas cleaning, and in various combinations. The sludges and dusts resulting therefrom are in the present state of the art special waste, which must be disposed of in a costly way by dumping. The volume of this special waste, measured as the output volume of the waste, is in fact small, yet dumping of residual materials from gas washing is an unsatisfactory solution:

- each special waste dump represents a residual risk for the environment, and

- industrially usable valuable materials are removed from the circulation of materials in the economy, as is desirable and required by legislation.

The object of the invention is therefore to indicate a method for recovery of useful materials from synthesis raw gas during gasification of waste, and thus to design the gasification of waste as being free of dumpable residual materials. A further object of the invention is to exclude stress on the environment due to waste water. Finally, it is also an object of the invention to indicate a device for carrying out the method according to the invention.

According to the present invention there is provided a method for total material emission-free utilisation of all the components of a community or industrial wastes by high-temperature recycling and by fractional material-specific conversion of the synthesis raw gas thus resulting, including at least the following process steps:

staged conversion of the materials contained as harmful material in the synthesis raw gas into material of value, in separate, separately heated wet-treatment stages, the temperature conditions of each treatment stage being predetermined by the stage condensation, necessary for the partial separation, of the water vapour contained in the synthesis raw gas,

bringing together the solutions and condensates containing the converted useful materials of the different conversion stages and staged separation of the recoverable useful materials by staged precipitation and ion exchange

reactions and separation reactions, with recovery of the process water, and

cold drying of the synthesis gas cleaned by the conversion of harmful materials, and return of the recovered process water together with the condensate from the cold drying to the individual conversion stages.
As regards the method, this object is achieved by the characterising part of claim 1 and the sub-claims indicate advantageous further developments thereof.

As regards the device, claim 12 indicates the solution with advantageous further developments in the sub-claims.

By the staged conversion of the contents appearing as harmful materials in the synthesis raw gas into usable materials in separate, separately heated wet-treatment stages, the condition is satisfied for the recovery of the materials, the conversion, i.e. the transfer of the materials into a recoverable form ,in separate, separately heatable wet-treatment stages, enabling conversion conditions adapted to optimum specific contained materials. The temperature of the treatment stages is in this case more appropriately predetermined by the staged condensation, necessary for the partial separation, of the water vapour contained in the synthesis raw gas. The contained materials converted into usable materials from the separate conversion stages are then recovered such that the solutions and condensates of the different conversion stages are brought together and

subjected in common to successively staged precipitation reactions and ion-exchange processes, with recovery of the process water. A subsequent cold drying of the synthesis gas cleaned of the undesirable ingredients removes the residual moisture which then, together with the covered process water, is again passed to the individual conversion stages, so that an enclosed lower process water circuit results. Thus, by virtue of the fact that firstly during cleaning of the synthesis raw gas, its ingredients are not only separated, but are converted before separation into a form which is directly reusable after separation, the condition is satisfied for a residue-free synthesis gas cleaning, and also in that the process water and the condensates of the conversion stages are subjected in common to staged precipitation and ion exchange reactions, this providing a simple possibility of recovering the useful materials, as their reactions in the conversion stages and the type of precipitation and ion-exchange reaction can be designed to be coordinated with one another.

Ingredients of the synthesis raw gas can if necessary be directly separated, i.e. without conversion, which then only comes under the sense of the inventive idea if the ingredient is industrially usable in this form. It can therefore be advantageous to dispose a catalytically-acting separately-operated separation stage in the flow path of the synthesis raw gas.

Such a possible separation exists for example for sulphur, which may be separated as an element with the aid of the catalytically-acting so-called "Sulferox" method and in this form is a material which is usable in many areas.

Preceding cleaning of the synthesis raw gas in the present state of the art there is usually a shock-type cooling directly after it leaves the high-temperature

reactor, in order to suppress a "de-novo" synthesis of organic harmful materials. In this case the synthesis raw gas flows through a water spray. According to the invention, this water spray, the so-called "quench" can be used as the first conversion stage, in that it is operated as a spray quench in the pH range of < 5, i.e. in the acidic range. Thus hydrogen chloride and heavy metals are converted into recoverable chlorides. After the acidic spray quench the synthesis raw gas passes through a neutralising, basically-adjusted wet-treatment stage. During this passage its temperature is optimally adjusted for the subsequent specific conversion stages. Thus a plurality of advantages arise:

The water vapour contained in the synthesis raw gas is condensed in the quench and does not prevent following conversions;

The water carried out of the spray quench is held back in the neutralising stage and is usable again due to the neutralisation;

The synthesis raw gas enters subsequent treatment stages at an optimum temperature, so that at that point the reactions are improved and accelerated.

It is particularly advantageous if the synthesis raw gas thus heated subsequently passes through several conversion stages, which are disposed in a common container which is however subdivided in accordance with the stages provided. Such an arrangement is described for example in European Patent No. 0 742 039 under the name "combination washer". Within this combination washer, a dust removal stage can more appropriately be disposed, more advantageously with a dust removal agent of a greater viscosity than water, for example glycerine. The dust removal agent is thus freed of dust and regenerated in its own circuit, the dust is

returned to the high-temperature reactor and at that point again participates in the gasification reaction. Thus the conversion, associated with the flow path of the synthesis gas, of the noxious elements contained therein, into recoverable useful materials, and their transfer into the waters of the various conversion stages, is terminated. The synthesis gas cleaned in this way of undesirable mixtures can, if necessary after an additional cold drying to remove any remaining residual moisture, after renewed heating of the dry synthesis gas with subsequent passage through an activated carbon filter, be returned for material and/or thermal utilisation. The cold drying can be effected in a separate treatment stage. It is advantageous to integrate this stage into the combination converter. The waste heat from this stage and from the spray quench can be de-coupled if required and used to equalise the temperature of the conversion stages, and to heat the gas.

The solutions and condensates of the conversion and cooling stages, which the usable materials to be recovered contain in solution, possibly also in dispersion, are brought together and further treated in common. Firstly, iron and heavy metals such as lead and zinc are separated in a staged hydroxide precipitation. The precipitated iron compounds from the first precipitation stage are more advantageously returned to the high-temperature reactor, are there melted down and removed as a usable metallic granulate. The mixed precipitations of the subsequent precipitation stages contain the other heavy metals and, processed into a concentrate, are a usable material capable of smelting.

The solution flowing from the hydroxide precipitations predominantly contains alkali chlorides. The residual portion of the calcium ions is precipitated by the introduction of carbon dioxide as calcium carbonate and

likewise returned to the high-temperature reactor for melting down. The disruptive calcium ions still remaining, which are present in a small proportion, and which would contaminate the alkali chloride usable salt, are removed in an ion exchanger. The alkali chloride solution thus cleaned is concentrated. For this purpose, more advantageously the solution is subjected to reverse osmosis. Finally, there is obtained in a crystallisation evaporator a mixed salt of use as a raw material and a condensate are obtained, which can be optionally used as operational water. Thus, by means of the method according to the invention, both the material utilisation of all gases, vapours and dusts leaving the high-temperature reactor and also total freedom from waste water are guaranteed.

A device preferably used for carrying out the method according to the invention according to claims 1 to 11 comprises a flow path for the synthesis gas, a recovery path for the converted usable materials and return devices to the high-temperature reactor and to the conversion stages. In this respect the flow path for the synthesis gas comprises at least after-treatment stages for

shock cooling with a pH value of <5,
neutralisation with a pH value of >8

and a combination converter, which if necessary includes further wet-treatment stages for conversion into recoverable usable materials, a glycerine dust wash, a Sulferox wash and a cold drying stage. The combination converter is then followed by a gas heating system and an activated carbon filter. In the sequence indicated, the synthesis raw gas flows through the flow path of the device and emerges as a high-purity thermally and/or materially usable synthesis gas. The recovery path, which serves to recover the converted usable materials, comprises at least

the reaction stages

hydroxide precipitation for iron,
hydroxide precipitation for other heavy metals,
carbon dioxide precipitation and
ion-exchanger for calcium,
reverse osmosis and
crystallisation evaporation,

through which the water laden with usable materials coming from the shock cooling passes in common through neutralisation and the conversion stages, after it has been collected and passed to the recovery path via the first hydroxide precipitation. The respective reaction stages of the recovery path have removal devices for the usable materials sulphur, heavy metal hydroxides, usable salt and usable gas, and return devices to the high-temperature reactor for the separated iron hydroxide and the dusts from the glycerine wash. The process water remaining after recovery of the usable materials is available as raw material water for optional use.

By means of a heat-coupling between shock cooling, gas temperature equalisation, cold drying and tempering of the conversion stages, the overall efficiency of the device can be improved, and for this purpose can have corresponding heat exchangers, and if necessary also heat pumps.

The invention will be described in more detail with reference to the Figure.

In this Figure, the number 1 indicates the high-temperature reactor, which as for example described in P 41 30 416, is operated as a melt-out reactor and has the outlets 19 and 20 for Fe and its alloy metals and the minerals which have been rendered inert, and the gas outlet

22 for the synthesis raw gas, which is passed into the spray quench 2. In this spray quench 2, which is operated in the pH range <5, i.e. in the acidic range, conversion of the ingredients begins, above all of Cl, Pb, Zn and Fe carried along. Simultaneously there takes place the shock-like re-cooling of the synthesis raw gas in order to prevent reformation of organic toxic materials (dioxins, furanes). Thereafter the synthesis raw gas is passed into the neutralisation bath 3 which, at a pH value of >8, neutralises the raw gas moisture. The pH value conditions in the spray quench 2 and in the neutralisation bath 3 are coordinated with one another; they are more appropriately continuously measured and adapted. After any necessary renewed gas heating 6′, which is predetermined by the reactor conditions of the mixed conversion stage, the synthesis raw gas passes into the combination converter 4, which, in addition to one or a plurality of conversion stages, has a glycerine wash for dust removal, a Sulferox stage for catalytic separation of sulphur and a stage for cold drying. The sulphur, in a form usable as a useful material, is removed through the outlet 16 directly from the Sulferox stage which is operated separately from the other (wet) conversion stages. The glycerine wash has for the separated dusts the outlet 8, by means of which the dusts which could be charged with noxious materials in an adsorbent manner, are returned for renewed high-temperature treatment in the reactor 1. After the cold-drying, the synthesis raw gas is heated (heating 6″) and, after passing through the activated carbon filter, leaves the device through the outlet 18 as a high-purity synthesis gas. A preferred embodiment here proposes to house the activated carbon filter in exchangeable cassettes through which gas can flow. In this way a simple exchange is possible, and the return of the activated carbon into the high-temperature reactor. The cassette can then be reused. The heat sources and sinks (6, 6′, 6″, cold drying) located in the described flow path are thus thermally coupled with the

aid of suitable elements such as heat exchangers and heat pumps, as symbolised by the number 16 and the directional arrows. The process water from the spray quench 2, neutralisation 3 and the combination converter 4 is collected and passed by means of the pipe system 7 to the first hydroxide precipitation 9. The iron hydroxide separated here is returned via the outlet 15 into the high-temperature reactor 1 and there melted down. Thereafter the collected process water passes through a second hydroxide precipitation 10, in which lead and zinc hydroxides are precipitated in common and are removed through the outlet 21 as a mixture. This mixture is known in technology to be usable as a raw and useful material capable of smelting.

In supplementation of the method procedure described, it is also possible, after the second hydroxide precipitation, to interpose an additional precipitation with $CO_2$ and to precipitate out any calcium ions present. Thereafter the process water contains mainly sodium and potassium chlorides, which as a usable material may only be slightly contaminated with calcium. These calcium impurities are removed in the ion-exchanger 11 and the alkali chlorides are concentrated in the reverse osmosis stage 12, before they are obtained as a usable salt in the crystallisation evaporator 13 and removed through the outlet 17. The process water is thus freed of its ingredients and can be optionally used, together with the condensate from the cold dryer as operational water. The process is free of waste water.

The Figure shows that when the inventive idea is used, gasification of waste is not only free of emission of toxic materials, but also can be carried out with total utilisation of the energy and material contents of the waste, without the occurrence of dumped residual material and without environmental stress due to waste water.

By means of the high-temperature recycling method proposed here, wastes of varying origins and composition are totally transformed into reusable materials, i.e. into

- mineral granulate,
- iron metal alloy,
- synthesis gas,
- distilled water,
- elementary sulphur,
- salt mixture capable of electrolysis, and
- zinc and lead concentrate

It will be clearly understood that, although a number of prior art publications are referred to herein, this reference does not constitute an admission that any of these documents forms part of the common general knowledge in the art, in Australia or in any other country.

For the purposes of this specification it will be clearly understood that the word "comprising" means "including but not limited to", and that the words "comprise" and "comprises" have a corresponding meaning.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for total material emission-free utilisation of all the components of a community or industrial wastes by high-temperature recycling and by fractional material-specific conversion of the synthesis raw gas thus resulting, including at least the following process steps:

staged conversion of the materials contained as harmful material in the synthesis raw gas into material of value, in separate, separately heated wet-treatment stages, the temperature conditions of each treatment stage being predetermined by the stage condensation, necessary for the partial separation, of the water vapour contained in the synthesis raw gas,

bringing together the solutions and condensates containing the converted useful materials of the different conversion stages and staged separation of the recoverable useful materials by staged precipitation and ion exchange reactions and separation reactions, with recovery of the process water, and

cold drying of the synthesis gas cleaned by the conversion of harmful materials, and return of the recovered process water together with the condensate from the cold drying to the individual conversion stages.

2. A method according to claim 1, in which at least one catalytically-acting, separately-operable separation stage is disposed in the flow path of the synthesis raw gas.

3. A method according to claim 1 or 2 in which the cold drying step takes place in a shock cooling stage wherein, the shock cooling stage is in the form of a spray

quench and is operated in a pH range of <5 for converting the hydrogen chloride and the heavy metals into recoverable chlorides.

4. A method according to claim 3 in which after the spray quench, which is adjusted to be acidic, the residual moisture of the synthesis raw gas is neutralised by a wet-treatment stage which is adjusted to be basic, and the synthesis raw gas is adjusted to an optimum temperature for the subsequent specific conversion stages.

5. A method according to any one of claims 1 to 4, in which there are a plurality of conversion stages disposed in a common but sub-divided container which forms a combination converter, and the synthesis raw gas flows through this combination converter at an approximately constant temperature.

6. A method according to claim 5, in which there is a particle separation stage within the combination converter and, if necessary, a separate circuit of the additive used is operated, wherein the separated particles are returned to degasification reaction.

7. A method according to any one of claims 1 to 6, in which iron and other heavy metals are recovered in succession from the combined solutions and condensates of the cooling and conversion stages by an at least two-stage hydroxide precipitation operation, in which the precipitated iron compounds are returned to the high-temperature reactor, are melted down there and removed as a metallic granulate, while hydroxides of the other heavy metals are processed as a concentrate capable of smelting, and are used directly as a raw or useful material.

8. A method according to claim 7 in which the other heavy metals include zinc and lead.

9. A method according to claim 7 or 8, in which the solution, predominantly containing alkali chlorides, flowing from the hydroxide precipitations, is freed of contaminating calcium ions in an ion exchanger.

10. A method according to claim 9, in which the purified alkali chloride solution flowing from the ion exchanger is concentrated by a reverse osmosis, and then there is obtained therefrom in a crystallisation evaporator a mixed salt of value as a raw material and a condensate of value as a process water.

11. A method according to any one of claims 5 to 10, in which associated with the shock cooling is a heat recover, in which the heat thus recovered is at least partly used for temperature equalisation of the synthesis gas and the conversion stages in the combination converter and if necessary for heating the gas in front of an activated carbon filter.

12. A device for carrying out the method according to any one of claims 1 to 11, including a flow path for the synthesis gas which contains at least the following active stages for wet-treatment:

- shock cooling with a pH value of <5,
- neutralisation with a pH value of >8, and
- a combination converter which integrally contains at least one converter stage for harmful materials, a glycerine wash, a Sulferox wash and a cold drying stage, and a
- gas heating system and an
- activated carbon filter

in the succession indicated, which further has a recovery path which contains at least the following reaction stages:

- hydroxide precipitation for iron,
- hydroxide precipitation for heavy metals,

- ion-exchange calcium,
- reverse osmosis and
- crystallisation evaporation,

through which the water laden with materials passes from shock cooling neutralisation and conversion in the sequence indicated, the reaction stages having removal devices for the useful materials water, usable gas, usable salt, sulphur, heavy metal hydroxides, iron and minerals, and return devices for iron hydroxide and carbon to the high-temperature reactor.

13. A device according to claim 12, in which a gas temperature-equalising system is disposed in the flow path of the synthesis gas between the neutralisation and the combination converter.

14. Device according to claim 12 or 13, in which the shock cooling includes a heat recovery system which is at least partly coupled with the gas heating, the gas temperature-equalising system, and the cold drying.

15. A device according to any one of claims 12 to 14, in which in succession there are disposed a feed device, a de-gassing channel and a high-temperature reactor, in which the high-temperature reactor has a removal opening for melts and a removal opening for the synthesis gas, after which there is incorporated a gas cleaning device.

16. A method for total material emission-free utilisation of all the components of a community or industrial wastes by high-temperature recycling and by fractional material-specific conversion of the synthesis raw gas thus resulting substantially as herein described with reference to the accompanying drawings.

17. A method according to claim 1, in which at least one catalytically-acting, separately-operable separation

stage is disposed in the flow path of the synthesis raw gas substantially as herein described with reference to the accompanying drawings.

Dated this 1st day of March 2001

THERMOSELECT AG

By their Patent Attorneys

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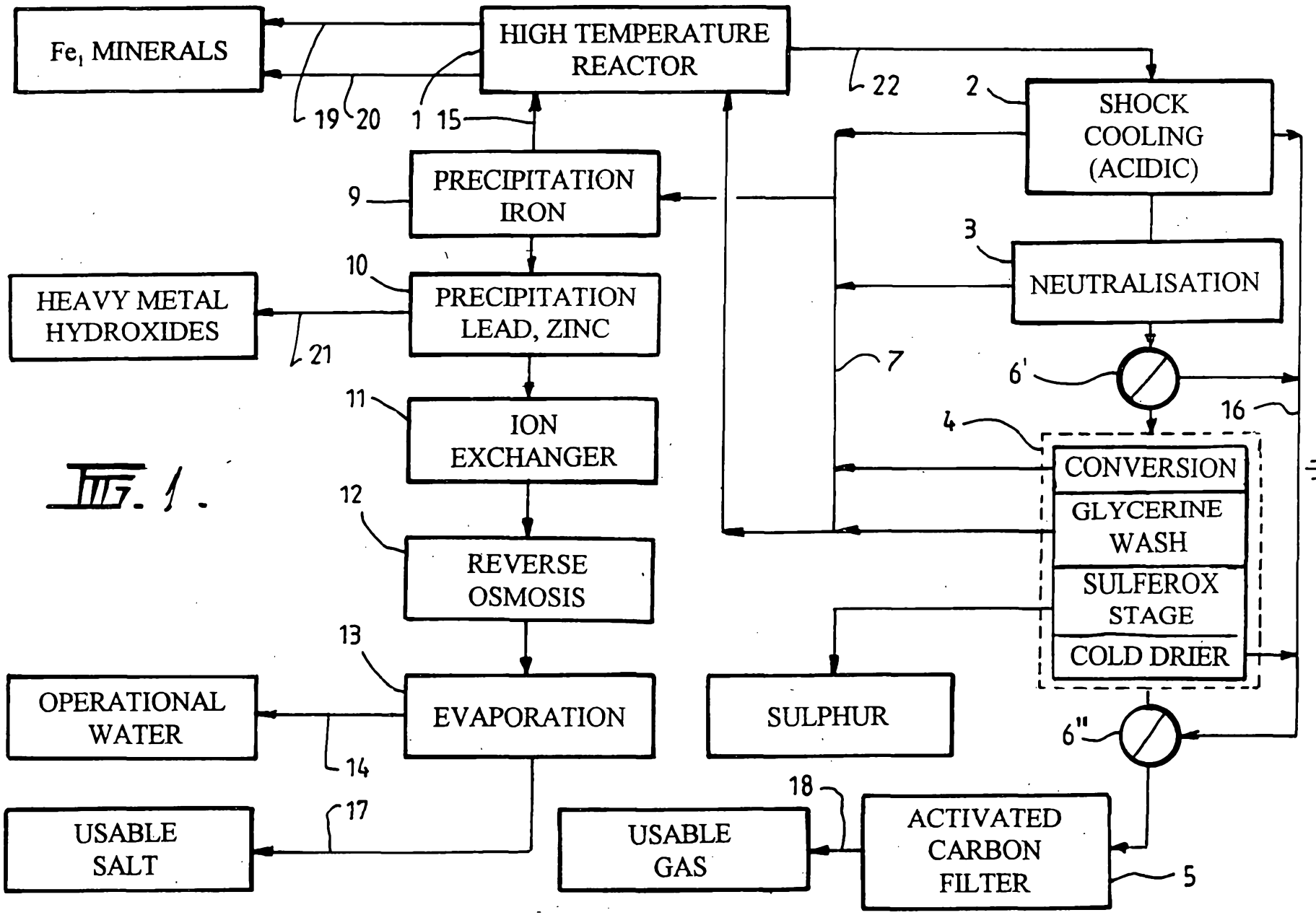


FIG. 1.

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