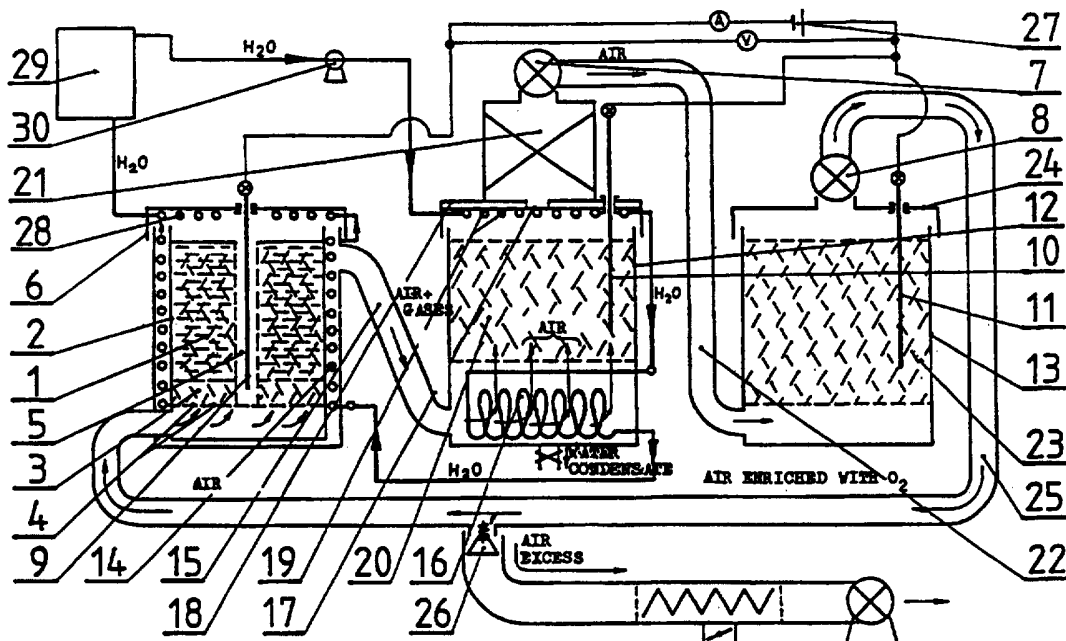




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(54) Title: METHOD AND INSTALLATION FOR THERMAL TREATMENT OF WASTE CONTAINING METALLIC COMPOUNDS



(57) Abstract

Metallic waste charge (1) on top of sawdust ignition layer (3) placed in a closed combustion chamber (2) supplied with oxygen enriched air through grid (4). Gases and vapours of combustion are cooled and purified in subsequent filter chambers (12, 13) and enriched with oxygen from anodes (10, 11) in an electrolytic circuit comprising a cathode (9) which generates hydrogen inside the combustion chamber (2). The treated gases are recycled back to the grid (4) as combustion air. The hydrogen reduces metallic oxides in the combustion reactions to reclaimable metals.

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METHOD AND INSTALLATION FOR THERMAL TREATMENT
OF WASTE CONTAINING COUMPOUNDS

A method of utilisation of wastes containing metallic compounds and the installation employing this method, used for utilising plating wastes, used paints, varnishes with mineral pigments, and other wastes containing metallic compounds are subject of the inventions.

Known is the method of utilising plating wastes, in which the waste, after being dried, is mixed with fine coal or coke breeze. Next, the mixture is burnt in a tunnel oven with gas as an additional source of energy. As a result of this process, one obtains a mixture of metallic oxides of low oxidation number. Such oxides, being water insoluble, can be safely stored. Patent application P-293647 of Siemens Company has, as the subject of inventions, an installation for thermal processing of wastes and the method of this processing in which the wastes to be utilised, in a form of metallic compounds, are subject to a far-reaching process of low-temperature carbonisation and without the access of oxygen. In this process low-temperature oven gas and low-temperature residue are formed. The latter is separated into fine- and coarse grained components. Fine-grained component and/or dry dust wastes and/or liquid wastes with low-temperature oven gas are burnt, producing combustion gases and molten slag, whereas coarse grained component is separated.

The solution according to P-263647 enables only to separate coarse grained assortment in a form of metallic alloy pieces. Non-utilised metallic

compounds, however, remain is slag. This method does not allow the recovery of pure metals from toxic metallic compounds subject to utilisation.

Patent application P-293027/PCT/NL 91/00058 puts forward a method of combined processing of wastes where a waste of relatively high energetic value is subject to the process of pyrolysis in order to obtain gas and/or oil with coal residue. Next, pyrolysis residuum is mixed with waste of a relatively low energetic value so as to form a mixture with water. The mixture that has been obtained is shaped into pieces until it gets the form of ceramic products. In order to enrich energetically the waste subject to pyrolysis the method proposes to add sawdust to it. This method does not make it possible to recover metals whose compounds are contained in utilised wastes.

Unknown are the methods of direct thermal recovery of pure metals from chemical metallic compounds contained in wastes subject to utilisation because of their harmfulness, e.g. precipitates or residue of plating baths, used or expired paints containing mineral pigments etc.

According to the invention, the method of thermal utilisation of wastes containing metallic compounds can be characterised by the fact that the waste with metallic compounds in a form of pulp with diluent content of 15 to 70% by weight is mixed with sawdust-waste coming from wood-processing, or with mixture of sawdust with wastes of highly flammable material, prepared in advance. The charge of this kind is put into a tightly-closed combustion chamber in oxidising-reducing conditions. The charge is then beaten down and some free space is left (cylindrical would be most proper) situated coaxially in relation to the axis of symmetry of the combustion chamber. The combustion chamber is then closed at the top. At

the bottom, under the grid, the process of combustion of ignition layer is initiated. Most suitable would be the layer of sawdust situated between the grid and the charge. With the access of air into the space under the grid and into the free space, the combustion chamber is tightly closed with a lid. The process of combustion results with complete burning out of the sawdust in the charge, while gases and steams are subject to a well-known process of refining and again, all or part of them, as air, are directed to the combustion chamber. The other version of this method suggests that the gases and steams refined in filter chambers are enriched with oxygen educed on the anodes placed in these chambers. Oxygen is obtained from gas products of the process of the charge combustion owing to a cathode located in the area of free space inside the charge in the combustion chamber, and anodes inside each of the filter chambers with closed cycle of gases, and feeding the electrodes, from constant voltage source of safe value, during this process, and maintaining current density on a constant level, most desirably ranging from 2 to 10 A/m². At the same time, in the combustion chamber, combustion is enriched with hydrogen, educed on the cathode, bonding a part of oxygen in the chamber and catalysing a reduction reaction of metallic oxides into metals.

The installation for thermal utilisation of wastes that contain metallic compounds is characterised by a hermetic combustion chamber in oxidising-reducing conditions with cooling coil installed around the chamber, on its full height, and within the lid. The bottom is provided with a grid under which the air inflow is situated. At the top the installation is equipped with the outlet of gases and steams tightly connected with the lower part of the first filter chamber where the cooling coil of gases and steams is embedded. The dry filter is over the cooling coil. The first filter

chamber is closed on its top with a lid having a cooling coil installed. In the lid there is also the outlet of refined gases connected, through a scrubber, with a fan that is, from its other side, joined with the inlet of the second filter chamber. The outlet of the second filter chamber is also connected with the pressure regulation valve and with the air inlet of the combustion chamber. In the other version of the invention, the combustion chamber is provided with a joint cathode. Each of the two filter chambers has an anode connected with the source of safe voltage of regulated initial current magnitude.

The solutions enable thermal utilisation of one of the most toxic wastes, like galvanic sludge or waste, paints and varnishes containing mineral pigments, in conditions propitious for recovery of metals contained in chemical compounds of these wastes. More important, these metals are recovered in a form of metallic powder. The method uses sawdust as the source of energy for the whole process. Sawdust, residual wastes from wood-processing, has also the function of an absorbent of pulp and is a means enabling to obtain, in the process of roasting, waste particles of temperature ranging from 1000°C to 1400°C. The method can be carried out in a closed cycle, in conditions of full ecological cleanliness of the process. Considerable amount of thermal energy is produced. The ash, being the remains of the process, after separation of pure metals in a form of powder, can be used as a high-quality binding agent, ecologically clean, useful for producing building elements of high mechanical and insulating parameters. The instances of the use of the installation presented on a draught - a scheme of the device - provide us with a more detailed description of the installation in the process of utilisation.

The waste in a form of pulp, subject to the process of utilisation, contained: SiO₂- 2,3%; Fe₂O₃- 2,0%; Al₂O₃- 0,3%; CaO- 10,5% MgO- 1,4%; Cr₂O₃- 27,8%; ZnO- 0,37%; NiO- 0,04%; PbO- 3,23%; CuO- 0,2%; CdO- 0,34%; and H₂O- 51,52% by weight.

The waste was mixed with small wood wastes, sawdust, with granulation from 0,3 to 10 mm at a weight ratio of one to one. Such formed a charge /1/ weighing 200kg is put into the combustion chamber /2/ on the ignition layer /3/ situated on the chamber's /2/ grid /4/. Before filling the chamber /2/ with the ignition layer /3/ of sawdust and with the charge, a section of a pipe of 100mm inside diameter is placed. After filling the chamber /2/, the charge /1/ is beaten down, layer by layer, and then the pipe is taken out in order to leave some free space /5/. Further on, under the grid /4/, the process of combustion of the ignition layer /3/ of sawdust is initiated. At the same time the air is let into the space under the grid /4/ and into free space /5/ inside the charge. The combustion chamber /2/ is tightly closed with the lid /6/. With the initiation of the process of combustion, after having closed the combustion chamber /2/ with the lid /6/, the fans /7,8/ are switched on. The circulation of gases and steams, coming from the process of combustion, is closed. The feeding steel cathode /9/ of constant safe voltage is turned on. This cathode /9/ is embedded in the lid /6/ of the combustion chamber /2/. In the process of performance the cathode /9/ is placed in free space /5/ within the charge /1/. Safe constant voltage feeds also the anodes /10,11/ embedded in the filter chambers /12,13/. Gases and steams, formed in the chamber /2/ and passing through free space /5/ and the cathode /9/, are subject to both the process of refining in the filter chambers /12,13/ and enrichment with oxygen enduced on the anodes /10,11/ in the filter chambers /12,13/. Simultaneously, on the cathode /9/ in the combustion

chamber /2/, hydrogen is reduced bonding part of oxygen in the chamber /2/ and catalysing a reduction reaction of metallic oxides into metals. Electrodes /9,10,11/ are fed with direct current of safe voltage, regulated in such a way as to maintain constant current density of 6,4 A/m². The process of combustion was carried out for 12 hours until complete combustion of sawdust in the charge /1/. The result of the process was obtaining 33,16 kg of ash with the content as follows: SiO₂- 3,32%; Fe- 6,03%; Al₂O₃- 0,3%; CaO- 21,12%; MgO- 1,2%; Cr- 56,69%; Zn- 0,21%; Ni- 0,01%; Pb- 8,75%; Cu- 0,48%; Cd - 0,9%; and C- 0,9% by weight.

In the first filter chamber /12/ 40,7 kg of water, containing chromium, zinc, lead and carbon, is obtained, which, together with the precipitation on filters, is put back to the next charge /1/ of the combustion chamber /2/. Finally, after pneumatic and magnetic separation in variable magnetic flux, the following elements are obtained from the charge: 1,9kgs of Fe; 18kgs of Cr; 6kgs of CaO; 2,7kgs of Pb; 0,15 kgs of Cu; and 0,26 kgs of Cd.

After separating metals, the remains undergo the process of homogenisation. As a result, materials with bonding hydraulic properties are obtained.

The installation for thermal utilisation of wastes containing metallic compounds is equipped with the combustion chamber /2/, surrounded on its full height with a cooling coil /14/ that is also installed in the lid /6/. On the bottom, over the air inlet inside the combustion chamber /2/, there is a grid /4/. On its top, the combustion chamber /2/ is tightly closed with the lid /6/ in which a steel cathode /9/ is embedded. When the combustion chamber /2/ is closed, the cathode /9/ is inside it, placed in the free space /5/ of the charge /1/. On its top the chamber /2/ is connected, through a cable /15/, with the lower part of the first filter chamber /12/ where the cooling coil

/16/ is embedded. Over it there is dry filter /17/ in which a graphite anode /10/ is placed. The first filter chamber /12/ is, on its top, tightly closed with a lid /18/ provided with a cooling coil /19/ and an outlet /20/ of refined gases and steams, connected through a scrubber /21/ embedded on the lid /18/, with a fan /7/ the outlet of which is joined, through a cable /22/ from the bottom, with the second filter chamber /13/ in which there is the dry filter /23/. The second filter chamber /13/, on its top, is tightly closed with a lid /24/ that has the outlet to the other fan /8/ connected, through a cable /25/, both to the pressure regulation valve /26/ and to the air inlet of the combustion chamber /2/, placed under the grid. In the lids /18,24/ of each of the filter chambers /12,13/ there are graphite anodes /10,11/ fed from the source of constant voltage /27/. The outlet of the cooling coil /14/ is connected, through the cooling coil /28/, with the heat receiver /29/ from which water, through a pump /30/ and the cooling coil /19/ goes to the inlet of the cooling coil /16/ placed in the lower part of this chamber /12/. The outlet of the cooling coil /16/ is connected with the inlet of the cooling coil /14/ surrounding the combustion chamber /2/.

PATENT CLAIMS

1. The method of thermal utilisation of wastes containing metallic compounds, in which the utilised waste is mixed with energy-carrying wastes on the way that the waste containing metallic compounds, in a form of pulp with diluant content of 15 to 70% by weight, is mixed with sawdust, which is a waste from wood processing, or with, prepared beforehand, a mixture of this sawdust and wastes of inflammable material, and then the charge /1/, formed in such a way, is placed in a tightly closed combustion chamber /2/ in oxidising-reducing conditions, beaten down, layer by layer, with some free space /5/, considering that cylindrical and formed coaxially in relation to the axis of symmetry of combustion chamber /2/ on its full height would be the most proper, and after that the process of combustion of the ignition layer /3/ is initiated under the grid /4/, considering that the layer of sawdust placed between the grid /4/ and the charge /1/ would be the best, simultaneously letting the air into the area under the grid /4/ and into the free space /5/, and then closing the combustion chamber /2/ with the lid /6/ in order to obtain complete combustion of sawdust in the charge /1/ and where gases and steams that are formed during the process are subject to the process of refinement and then, as air, are carried back to the combustion chamber /2/.

2. The method described in the preceding patent claim, characteristic by the fact, that gases and steams are refined in the folter chambers /12,13/ and enriched with oxygen educed on the anodes placed in the filter chambers /12,13/, where the oxygen comes from gas products of the charge

combustion /1/, which is made possible by placing the cathode /9/ in free space area /5/ inside the charge /1/ in the combustion chamber /2/, and the anodes /10,11/ inside each of the filter chambers /12,13/ of the closed circulation of gases, and feeding the electrodes /12,13/ during the process of combustion from safe, constant voltage source, maintaining constant level of current density, the most appropriately at the level from 2 to 10 A/m², while the combustion /2/ is simultaneously enriched with hydrogen which bonds part of oxygen in the combustion chamber /2/ and catalyses the reduction reaction of metallic oxides into metals.

3. Installation for thermal utilisation of wastes containing metallic compounds provided with known filter chambers, characteristic by the fact that it is the close combustion chamber /2/ with oxidising-reducing conditions, surrounded on its full height by cooling coils /14/ placed also on the lid, and on the bottom equipped with the grid /4/ under which there is the air inlet, and on its top having the outlet of gases and steams tightly connected through a cable /15/ to a lower part of the first filter chamber /12/ in which the cooling coil /16/ for gases and steams is also placed with the dry filter /17/ situated over the cooling coil /16/, whereas the first filter chamber /12/ is hermetically closed on its top with the lid /18/ provided with the cooling coil /19/ and the outlet /20/ of refined gases connected through a scrubber /21/ with a fan /7/ and from its other side, through a cable /22/, connected with the inlet of the second filter chamber /13/, the outlet of which is joined, through another fan /8/, to the pressure regulation valve /26/ and to the air inlet of the combustion chamber /2/.

4. Installation described in the preceding patent claim No.3 characteristic by the fact, that in the combustion chamber /2/, a joint cathode /9/ is embedded, whereas in each of the two filter chambers /12,13/ there is the anode /10,11/ connected to the source of safe voltage /27/ with regulated output current variable.

