

METHOD OF ROASTING MATERIAL CONTAINING AT LEAST ONE OF V, MO
AND NI AND ROTARY KILN FOR ROASTING THE SAME

TECHNICAL FIELD

[0001]

The present invention relates to a method of roasting a material containing at least one of V (Vanadium), Mo (Molybdenum) and Ni (Nickel), which contains C (Carbon) and S (Sulfur) components, by oxidizing roasting to remove the C and S components therefrom before reducing the material with a reducing agent for recovery of a valuable metal of at least one of V, Mo and Ni.

TECHNICAL BACKGROUND

[0002]

In boilers that use petroleum fuel as fuel like in electric power plants, boiler sludge is deposited on the bottom of a boiler and dust collectors catch boiler ash. In the boiler sludge and boiler ash, heavy metals such as Ni and V are condensed as oxides. In ammonium metavanadate which is obtained by performing wet alkali treatment with the boiler ash, a heavy metal of V is condensed as an oxide.

[0003]

In the field of oil refinery, gas processing industry and others, desulfurization catalyst is spent in the refinery process. Once spent in this process, the desulfurization catalyst also contains, as oxides, heavy metals of Ni, Mo, and

V in the form of condensation. It is desired to recover these oxides, which are Ni, Mo and V, in the form of metal, which promotes more effective use of waste materials.

[0004]

As one of techniques for recovering valuable metals from those V, Mo and Ni containing materials, the inventors have proposed a method of recovering a valuable metal, the method including a roasting step of roasting a V, Mo and Ni containing material; a step of charging a heating furnace with the V, Mo and Ni containing material, a reducing agent and flux and heating them for reduction thereby to produce a V-containing slag and a Fe-Mo-Ni base alloy; and a step of charging a reducing agent for the V-containing slag to produce an Fe-V base alloy and a $\text{CaO-Al}_2\text{O}_3$ slag (see Patent document 1, claim 1).

[0005]

In this valuable metal recovering method disclosed in the patent document 1, the C and S components in the V, Mo and Ni containing material are first removed as oxides in the roasting step, and then the reducing agent is used to reduce the V, Mo and Ni containing material to produce a Fe-Mo-Ni base alloy. This reduction is followed by desulfurization and decarbonization of the Fe-Mo-Ni base alloy. The desulfurization and decarbonization are in compliance with the standards, applied in the field of steel handling Fe-Mo-Ni base alloy, which requires the sulfur component to be lowered.

[0006]

Patent document 1: Japanese Patent Laid-open (unexamined)

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DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007]

However, the step for the desulfurization and decarbonization of the Fe-Mo-Ni base alloy becomes complicated, because this step is carried out after a further step of supplying the Fe-Mo-Ni base alloy to the heating furnace and adding lime, $\text{CaO-Al}_2\text{O}_3$ base flux and $\text{CaO-Al}_2\text{O}_3\text{-FeO}$ base flux to stir them together. In addition, the desulfurization/decarbonization step involves a process to dispose of a desulfurizing material. These drawbacks result in an increase in recovery cost, thus making it difficult to realize recycling business. Moreover, the desulfurization and decarbonization of the Fe-Mo-Ni base alloy have limitations in their performances, which sometimes prevents the alloy from meeting the standards due to amounts of carbon and sulfur components contained in the Fe-Mo-Ni base alloy.

[0008]

Hence, in realizing the process for reducing V, Mo and Ni containing material with the use of reducing agents in order to recover the valuable metals, it is significant that S and C components are removed, as much as possible, from the V, Mo and Ni containing material in the roasting step preceding the reduction step. Furthermore, the sublimation of the Mo content in the roasting process results in a decrease in

recovery rate of the Mo content. Accordingly, it is necessary to take notice of the sublimation of the Mo content.

[0009]

The present invention has been made in view of the foregoing conventional problems, and it is an object to provide a roasting method and a rotary kiln which are able to reduce both C and S components in minerals down to 0.5 % or less, respectively, and secure a yield ratio of 90% or more for the Mo component.

MEANS FOR SOLVING THE PROBLEMS

[0010]

In order to resolve the foregoing problems, the inventors carried out experiments with a variety of types of rotary kilns. The results of the experiments made the inventors notice the order of the decarbonization and desulfurization generated within the roasting furnace. In other words, the fact is that the desulfurization will follow the decarbonization, i.e., on the contrary, there is little possibility that the desulfurization is generated so long as the decarbonization is generated (because the desulfurization is a reaction which is generated in an oxide atmosphere and whenever there remains a C component, oxygen is used for the decarbonization). The inventors' founding is that, when a material roasted is first subjected to oxidization of the C component in a material-charge-side zone in a roasting furnace and then to oxidization of the S component in a zone ranging from a central

zone to a material discharge side in the roasting furnace, a reaction time for making the S component oxidized can be prolonged, which ultimately leads to a large reduction in both the C and S components of the mineral roasted.

[0011]

Practically, as one aspect, the present invention provides a method of roasting a material containing at least one of V, Mo and Ni to remove C and S components from the material comprising oxidizing and roasting the material in a rotary kiln, before reducing the material by means of a reducing agent so as to recover a valuable metal comprising at least one of V, Mo and Ni, the method comprising steps of: charging the material containing the C and S components into a material charge side of a roasting furnace on which a burner is disposed; and taking an oxygen-containing gas taken into the roasting furnace to become parallel to a direction along which the material moves in the roasting furnace.

[0012]

As another aspect, the present invention provides a rotary kiln for roasting a material containing at least one of V, Mo and Ni to remove C and S components from the material by oxidizing and roasting the material in the rotary kiln, before reducing the material by means of a reducing agent so as to recover a valuable metal comprising at least one of V, Mo and Ni, the rotary kiln comprising: a roasting furnace into which the material containing the C and S components is charged as a material to be processed; a burner disposed on a material

charge side of the roasting furnace; and a line introducing an oxygen-containing gas into the roasting furnace, and wherein a direction along which the material moves in the roasting furnace and a flow of the oxygen-containing gas taken into the roasting furnace are set to be parallel with each other.

EFFECTS OF THE INVENTION

[0013]

According to the inventions of claims 1 and 10, as the material-charge-side zone in the roasting furnace is already in a high temperature atmosphere when a material to be roasted is charged into the furnace, the C component is first oxidized in the material-charge-side zone in the roasting furnace, and then the S component is oxidized in the zone ranging from the central zone to the material discharge side in the roasting furnace. The reaction time for oxidizing the S component can therefore be made longer, whereby both the C and S components in the mineral roasted can be reduced largely.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

Fig. 1 is a system diagram illustratively showing the overall configuration of an operation facility in which the roasting method of V, Mo and Ni containing materials according to the present invention is reduced into practice;

Fig. 2 is a diagram outlining a counter-flow type rotary

kiln according to a comparative example;

Fig. 3 is a graph showing a functional comparison between a parallel-flow type rotary kiln and a counter-flow type rotary kiln;

Fig. 4 is a sectional view outlining a rotary kiln according to the present invention;

Fig. 5 is a sectional view of a roasting furnace of the rotary kiln;

Fig. 6 is a flowchart showing how to recover valuable metals; and

Fig. 7 is a sectional view of the rotary kiln according to an embodiment.

In the boiler ash, by way of example, some 80 wt% of C component is contained, but no Mo component is contained. The carbon base sludge contains moisture, for example, by 50 wt%. As exemplified, waste materials with various types of components can be handled as a material to be roasted. Such materials are given with heavy fuel oil or moisture adhering thereto.

[0019]

Fig. 1 is a system diagram illustratively showing the overall configuration of an operation facility for putting the roasting method of a V, Mo and Ni containing material into practice. Materials are persevered, type by type, in hoppers 1 for materials to be processed. At a lower part of each of the hoppers 1, there is equipped with a volumetric feeder 2 so that the feeder 2 feeds, on a volumetric basis, a predetermined amount of each material to the carrying conveyer 3. In each volumetric feeder 2, the components of each material are adjusted. The carrying conveyer 3 conveys the volumetric-fed material to a material-accepting hopper 4. This material-accepting hopper 4 is equipped, at its lower part, with a material stirring feeder 5 which is a screw conveyer. The material stirring feeder 5 operates to stir the material and supplies it to a mineral-supplying chute 6 in a dropping manner. The mineral-supplying chute 6 receives the dropped material and guides the received material to a roasting furnace 8 arranged in a rotary kiln 7.

[0020]

The kiln includes a vertical type kiln, but in the present

invention, a horizontal type rotary kiln is selected for the rotary kiln 7. The material is composed of a solid form material, mud form material, or powder form material, or a mixture of those materials. The mixture is in almost sludge.

[0021]

The rotary kiln 7 is provided with the foregoing roasting furnace 8 for performing oxidizing roasting of a V, Mo and Ni containing material and a secondary combustion chamber 9 for secondarily burning exhaust gas. The roasting furnace 8 is produced in a cylindrical shape, on outer circumferential surface of which gears 18 are disposed. This roasting furnace 8 is configured to be driven by an electric motor which is not shown in the drawings. In addition, with the object of allowing the material to move from a material charge side 8a to a material discharge side 8b in the roasting furnace 8, the furnace 8 is paced to have a tilt so that the material discharge side 8b becomes lower than the material charge side 8a. Both the roasting furnace 8 and the secondary combustion chamber 9 are linked to each other so that the roasting furnace 8 is rotatable and the linkage therebetween is kept in an airtight manner. The exhaust gas discharged from an outlet of the roasting furnace 8 is guided to the secondary combustion chamber 9, where the guided exhaust gas rises up along the chamber 9. After being secondarily burned in the secondary combustion chamber 9, the exhaust gas is rendered harmless by familiarities including a waste heat recovery facility, exhaust gas cooling facility, exhaust gas processing facility

and dust collecting facility and then discharged outside.

[0022]

The mineral-supplying chute 6 is linked to a charging inlet which is formed in a front wall 10 which is an axially end face on the material charge side 8a of the roasting furnace 8. A burner 11 is arranged to pass through this front wall 10. Thus the burner 11 emits flame from the front wall 10 downstream in the roasting furnace 8. Coupled to the burner 11 are both a fuel supply line 12 and a combustion air line 13. Hence, a fuel pump 14, which intervenes between a fuel tank 15 and the line 12, operates to supply fuel such as heavy fuel oil from the fuel tank 15 to the burner 11. Moreover, the burner 11 receives supply of combustion air from a blower 16 via the line 13.

[0023]

The material charge side 8a of the roasting furnace 8 is linked with an air supply line 17 serving as a line for introducing a gas containing oxygen.

the air cools down the inside of the furnace and the in-furnace temperatures will be dropped largely, thus increasing the amount of the exhaust gas. Hence the air ratio is set to 2.5 or less. The air ratio is a ratio between an amount of air to be introduced into the rotary kiln and an amount of air necessary for oxidizing flammable components in the material and a ratio of 1.0 is equivalent weight. The flammable components in the material are C, H, N and S.

[0037]

As pictorially shown in Fig. 5, the roasting furnace 8 should partially be charged with the material. For example, an occupying percentage (filling degree) of the material to a cross section area of the roasting furnace 8 is 12 % or less. Only the surface of the material introduced into the roasting furnace 8 is permitted to touch the air. Thus, the greater the filling degree, the smaller the specific surface area of the material, providing no sufficient touch of the material to the air. It is therefore proposed that the filling degree be set equal to or less than 12 %. However, it should be avoided to give an extremely small value to the filling degree, because the production efficiency is obliged to be lessened.

[0038]

It is also desired that a gas flow speed within the roasting furnace 8 be set to 3 m/s or less. Dust whose specific gravity is small, such as boiler ash, may fly to the dust collector together with the exhaust gas, without being burned out sufficiently. Thus, in order to alleviate this problem,

it is desired that the gas flow speed in the furnace 8 be suppressed down to a smaller value.

[0039]

How to recover valuable metals composed of V, Mo and Ni will now be described, which involves heating the roasted minerals in a heating furnace after the oxidizing roasting and reducing the heated roasted minerals with reducing agents.

[0040]

Fig. 6 shows a flowchart for describing how to recover valuable metals. First, the roasted metals, reducing agents, and lime serving as flux are charged into an electric furnace serving as a heating furnace (step S1). The heating and reduction in the electric furnace produces a V-containing slag and an Fe-Mo-Ni base alloy.

[0041]

The Fe-Mo-Ni base alloy is separated from the V-containing slag, and then the Fe-Mo-Ni base alloy is subjected to desulfurization, dephosphorization, and decarbonization. The P component in the material remains in the Fe-Mo-Ni base alloy. Since tightened standards are applied to the S component, the desulfurization is required. Further, the decarbonization is also required, because the C component is recarbonized from electrodes. Through this process, the Fe-Mo-Ni base alloy is poured into a ladle furnace serving as a heating container (step S2). Then, the lime, $\text{CaO-Al}_2\text{O}_3$ base flux, and $\text{CaO-Al}_2\text{O}_3\text{-FeO}$ base flux and others are changed into the furnace for the desulfurization,

dephosphorization, and decarbonization. It is effective to use blowing an Ar gas and O_2 (utilizing a bubbling). However, when the oxidizing roasting process allows the decarbonization and desulfurization to be done sufficiently, these desulfurization, dephosphorization, and decarbonization processes can be omitted. Finally, the Fe-Mo-Ni base alloy that has experienced the desulfurization, dephosphorization, and decarbonization is cast into a mold.

[0042]

Meanwhile, the V-containing slag is also poured into a ladle furnace serving as a heating container (step S4). An Al-reducing agent, lime and V_2O_5 for adjusting the V component are also poured into this ladle furnace,

What is claimed is:

1. A method of roasting a material containing at least one of V, Mo and Ni to remove C and S components from the material comprising oxidizing and roasting the material in a rotary kiln, before reducing the material by means of a reducing agent so as to recover a valuable metal comprising at least one of V, Mo and Ni, the method comprising the steps of:

charging the material containing the C and S components into a material charge side of a roasting furnace on which a burner is disposed; and

taking an oxygen-containing gas into the roasting furnace to become parallel to a direction along which the material moves in the roasting furnace.

2. The method of claim 1, wherein the material is oxidized and roasted at an in-furnace temperature of 800 °C - 950 °C inclusive and an in-furnace retention time of 2 hours or more.

3. The method of either claim 1 or 2, wherein the burner comprises a short-flame burner for raising temperatures in a zone located on the material charge side in the roasting furnace and a long-flame burner for raising temperatures in a central zone of the roasting furnace and

the rotary kiln is equipped with a counter burner for raising temperatures in a zone on a material discharge side in the roasting furnace.

4. The method of any one of claims 1 to 3, wherein a cooling water nozzle is provided on the material charge side of the roasting furnace so as to spray water inside the roasting furnace.

5. The method of any one of claims 1 to 4, wherein the oxygen-containing gas is air,

an air ratio between an amount of air taken into the rotary

kiln and an amount of air necessary for complete combustion of a flammable component contained in the material is set to 1.5 to 2.5.

6. The method of any one of claims 1 to 5, wherein an occupying percentage (filling degree) of the material to a sectional area of the roasting furnace is equal to or less than 12 %.

7. The method of any one of claims 1 to 6, wherein a speed of the flow of the gas is 3 m/sec or less.

8. The method of any one of claims 1 to 7, wherein the rotary kiln is equipped with a dichotomized-type material discharge outlet at which the material is separated into a roasted mineral and a floatable dust.

9. The method of any one of claims 1 to 7, wherein the material discharged from a material discharge outlet of the rotary kiln is screened in particle sizes thereof to produce both coarse particle substances and fine particle substances; the coarse particle substances are then charged as a material into a heating furnace in a reduction process of reducing of the material by means of the reducing agent; and the fine particle substances are then subjected to processing which is either charging into the rotary kiln again as the material to be processed for the roasting or ultimate disposal.

10. A valuable metal recovery system for recovering a valuable metal comprising at least one of V, Mo and Ni, comprising:

a heating furnace for reducing a material containing at least one of V, Mo and Ni by means of a reducing agent; and

a rotary kiln for, before reducing of the material, roasting the material to remove C and S components from the material comprising oxidizing and roasting the material, the rotary kiln including:

a roasting furnace into which the material containing the

C and S components is charged as a material to be processed;
a burner disposed on a material charge side of the roasting furnace; and

a line introducing an oxygen-containing gas into the roasting furnace, and

wherein a direction along which the material moves in the roasting furnace and a flow of the oxygen-containing gas taken into the roasting furnace are set to be parallel with each other.

11. A rotary kiln for roasting a material containing at least one of V, Mo and Ni to remove C and S components from the material comprising oxidizing and roasting the material, before reducing the material by means of a reducing agent so as to recover a valuable metal comprising at least one of V, Mo and Ni, the rotary kiln comprising:

a roasting furnace into which the material containing the C and S components is charged as a material to be processed;
a burner disposed on a material charge side of the roasting furnace; and

a line introducing an oxygen-containing gas into the roasting furnace, and

wherein a direction along which the material moves in the roasting furnace and a flow of the oxygen-containing gas taken into the roasting furnace are set to be parallel with each other,

the burner comprises a short-flame burner for raising temperatures in a zone located on the material charge side in the roasting furnace and a long-flame burner for raising temperatures in a central zone of the roasting furnace and

the rotary kiln further comprises a counter burner for raising temperatures in a zone on a material discharge side in the roasting furnace.

12. A rotary kiln for roasting a material containing at least one of V, Mo and Ni to remove C and S components from the material comprising oxidizing and roasting the material, before reducing the material by means of a reducing agent so as to recover a

valuable metal comprising at least one of V, Mo and Ni, the rotary kiln comprising:

a roasting furnace into which the material containing the C and S components is charged as a material to be processed;

a burner disposed on a material charge side of the roasting furnace; and

a line introducing an oxygen-containing gas into the roasting furnace, and

wherein a direction along which the material moves in the roasting furnace and a flow of the oxygen-containing gas taken into the roasting furnace are set to be parallel with each other,

a cooling water nozzle is provided on the material charge side of the roasting furnace so as to spray water inside the roasting furnace.

13. The valuable metal recovery system of claim 10, wherein the rotary kiln further comprises a dichotomized-type material discharge outlet at which the material is separated into roasted minerals and a floatable dust.

14. The rotary kiln of claim 11 or 12, further comprising a dichotomized-type material discharge outlet at which the material is separated into roasted minerals and a floatable dust.