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(54) Titre : PROCEDE POUR DISSOUDRE DES CONCENTRES D'OXYDE DE MOLYBDENE

(54) Title: PROCESS FOR DIGESTING MOLYBDENUM OXIDE CONCENTRATES

(57) Abrégé/Abstract:
The present invention relates to a method for solubilizing poorly soluble molybdenum oxide concentrates under oxidizing conditions in basic media.

Abstract

The present invention relates to a process for digesting sparingly soluble molybdenum oxide concentrates under oxidizing conditions in basic media.

Process for digesting molybdenum oxide concentrates

The present invention relates to a process for digesting sparingly soluble molybdenum oxide concentrates and oxidizing conditions in basic media.

The prior art discloses various molybdenum-containing raw materials. They differ only slightly in the molybdenum content and the gangue composition. However, the mass ratio of the molybdenum oxides is very different. There are molybdenum raw material qualities which contain up to 50% molybdenum dioxide (MoO_2) and other sparingly soluble molybdenum suboxides, e.g. $Mo_4O_{11,}$ These raw materials are used to date predominantly in the steel industry since the hydrometallurgical conversion of such molybdenum raw materials into high-quality molybdenum compounds and finally into molybdenum metal is not possible under economical conditions.
In the production of molybdenum and molybdenum compounds in the chemical industry, exclusively raw materials which have a very high molybdenum trioxide content (MoO_3) and are very readily soluble in aqueous media are used at present. In view of the increasingly scarce high-quality raw materials and increasing raw material prices, any possibility of using alternative raw materials for molybdenum extraction which have an economic advantage should be investigated.
In most cases, molybdenite (MoS_2) serves as a molybdenum source. Molybdenite is usually converted into molybdenum oxide by roasting under oxidizing conditions. The molybdenum oxides thus obtainable, also referred to as technical molybdenum oxides, are digested by the known processes.
DE 2162065 is concerned with a process for purifying and digesting roasted molybdenum concentrates, also referred to below as technical molybdenum oxides. There, the technical molybdenum oxide is treated with a nitric acid which contains ammonium nitrate (NH_4OH). The content of free nitric acid results in a sufficient decrease in the impurities and the further digestion of the Mo compounds, so that, on subsequent dissolution in NH_4OH or NaOH, a comparatively smaller amount of residue on dissolution having a comparatively lower molybdenum content is obtained than on dissolution of untreated molybdenum concentrate.

A similar process is described in US 4 525 331. Here too, a nitric acid (HNO_3) excess is employed in order firstly to achieve better solubility of the impurities and secondly to oxidize residues of Mo(IV) into Mo(VI). The solid is then dissolved in NH_4OH.

US 4 596 701 proposes digesting the molybdenum oxides with an aqueous solution of sulphuric acid, ammonium sulphate and ammonium peroxodisulphate in order better to dissolve the impurities. Furthermore, the peroxodisulphate also oxidizes Mo(IV) still present to Mo(VI), so that a better molybdenum yield is achieved in the subsequent dissolution step with NH_4OH.

Another process for the preparation of high-purity alkali metal molybdate, which is described in US 4046852, envisages mixing the roasted molybdenum concentrate in a first step with mineral acids, the mineral acid being used in a stoichiometric excess, based on the impurities. In a second step, the suspension thus formed is treated in an autoclave at between 150°C and 350°C in the presence of free oxygen, impurities going into solution and Mo suboxides being converted into MoO_3. In the third step, the solid separated off is dissolved in alkali metal hydroxide.

DE 2345673 discloses a process for the preparation of high-purity molybdenum oxide and ammonium molybdate, the molybdenum oxide concentrate first being treated with an aqueous ammonium hydroxide solution for producing a suspension. The suspension thus obtained is then digested in the presence of free oxygen which is sufficient to convert the predominant proportion of the molybdenum oxides into soluble ammonium molybdate compounds. The residue, which still has proportions of molybdenum, is leached again with an aqueous alkaline solution which contains sodium hypochloride, at pH 9 to pH 10, in order to dissolve the remaining proportions of molybdenum.

In the abovementioned processes, separating off the impurities on digestion of the roasted molybdenum concentrate is of primary importance. Excessive reagent or addition of oxidizing agents relates primarily to the amount of impurities detected in the molybdenum oxide. The increase in the Mo dissolution yield on digestion of molybdenum concentrate by oxidation of the Mo suboxides during the digestion process is mentioned as a side effect. Molybdenum suboxide is oxidized to MoO_3 only in an amount which corresponds to the stoichiometry of the amount of oxidizing agent used.

With the use of free oxygen as an oxidizing agent, an autoclave is employed at at least 150°C and a pressure of about 7 bar. In the case of digestion of molybdenum concentrates with NH_4OH at atmospheric pressure in the presence of free oxygen, it is necessary to employ a plurality of steps in order to achieve a satisfactory molybdenum yield.

In all abovementioned processes, starting materials are used which either contain a very high proportion of molybdenum trioxide (MoO_3) soluble in aqueous media or consist exclusively of a contaminated molybdenum trioxide.

Starting from the prior art, it is the object of the present invention to provide an economical process which makes it possible to digest molybdenum oxide concentrates having a high proportion of sparingly soluble molybdenum oxides of up to 50% or more in a one-stage process with yields greater than 98%.

The invention is based on the surprising discovery that the sparingly soluble molybdenum oxide concentrates are virtually completely digested in aqueous suspension with hydroxides of the alkali metals (alkali solution) with simultaneous introduction of an oxidixing agent.

The object of the present invention is achieved by a process for digesting sparingly soluble molybdenum oxide concentrates, comprising the following steps:

a) suspending of the sparingly soluble molybdenum oxide concentrate in an aqueous solution,

b) metering of alkali solution of the alkali metals selected from the group (Na, K, Li) and/or mixtures thereof into the suspension from step a) and establishment of a desired pH, with stirring, an oxidizing agent simultaneously being introduced, and

d) production of a molybdenum-containing product which contains at least 98% of the molybdenum used.

Technical molybdenum oxide is a mixture consisting of MoO_3 and sparingly soluble MoO_2, Mo_4O_{11} with a proportion of MoO_2, Mo_4O_{11} of 2 to 65% by weight. Usually, the technical molybdenum oxide contains up to 50% by weight of sparingly soluble molybdenum oxides. The technical molybdenum oxides may contain up to 40, 30 or up to 20% by weight of the sparingly soluble molybdenum oxides.

In the process according to the invention, the molybdenum oxide concentrates are first suspended in water, preferably in demineralized water. Thereafter, an alkali solution having a concentration of up to 50% by weight, preferably up to 45% by weight, particularly preferably up to 40% by weight, is added until a desired pH is established and simultaneously, with stirring, an oxidizing agent is introduced so that a particularly homogeneous distribution is ensured in the entire reaction space.

The process according to the invention can be carried out in the stirred reactors known from the prior art. What is important here is that the flow conditions are adjusted so that an optimum distribution of the oxidizing agent in the suspension in the reactor is ensured. The oxidizing agent can be metered in at any point of the reactor, preferably directly below the stirring member. All customary stirrer types (paddle stirrer, disc stirrer, propeller stirrer) can be used for achieving a homogeneously mixed reaction zone in the reactor. The stirring speed may be up to 3000 rpm, preferably up to 2000 rpm. Particularly good results are obtained with the use of a disc stirrer at a stirring speed of up to 1000 rpm. The process according to the invention can be operated discontinuously (batchwise) or continuously. In a preferred embodiment, the process according to the invention is carried out in such a way that gases from the group consisting of air, oxygen, ozone and/or mixtures thereof are used as oxidizing agents. The gaseous oxidizing agents can be introduced into the reactor at any point, but preferably below the stirring member.

Good digestion results are obtained if a microfine distribution of the small gas bubbles in the suspension is present. This can be achieved by the use of a paddle stirrer, for example phase jets from Ekato. In this embodiment of the present invention, an Mo yield of 98% can be achieved after a duration of reaction of at least 6 hours at a pH of 9. At a pH of ≥ 12, the duration of the reaction decreases to ≤ 3 h. Liquid compounds, such as hydrogen peroxide, peroxodisulphates of the alkali metals and/or mixtures thereof can also be used as oxidizing agents. The process according to the invention is preferably carried out in such a way that the amount of oxidizing agent added is at least the stoichiometric amount, based on the MoO_3. Particularly preferably, the amount of oxidizing agent is at least a majority of the stoichiometric amount, based on MoO_3.

The stoichiometric amount may be at least two-fold, preferably at least three-fold.

A desired pH can be established in the reaction zone of the reactor, depending on the content of sparingly soluble molybdenum oxides in the molybdenum oxide concentrate. The pH is preferably at least 8, particularly preferably at least 10, especially preferably at least 11.

The digestion of the molybdenum oxide concentrates in the suspension is effected at temperatures which are sufficient to convert the sparingly soluble molybdenum oxides into MoO_3 and subsequently into a molybdate, e.g. sodium molybdate. The temperature is preferably at least 30°C, particularly preferably at least 50°C, especially preferably at least 60°C. In a further preferred embodiment of the process, the temperature is at least 70°C. The highest digestion rate is achieved if the temperature is at least 80°C, preferably at least 90°C. The molybdenum-containing products obtainable after the digestion are converted by the known processes into end products, e.g. molybdic acid, molybdenum metal or molybdenum salts.

The invention is further explained by the following examples.

Examples

Example 1

2.1 litres of demineralized water were introduced into a heatable 4 litre stirred reactor. 1790 g of technical molybdenum oxide having an Mo content of 62% and a proportion of MoO_3 of 60% were added with stirring so that a homogeneous suspension formed. The reactor cover with aeration tube was placed on top. Oxygen was introduced into the stirred reactor via a lateral inlet tube at a volume flow rate of 100 l/h (litre/hour). The oxygen feed was effected directly below the stirring member in order to ensure a good distribution of the small oxygen bubbles in the suspension. The stirring member was equipped with a paddle stirrer. The stirring speed was 1675 rpm. Thereafter, NaOH was passed in via a pump having a measuring and control unit continuously until a stable pH of 9.0 was reached. The suspension was heated via a double jacket with external heating circulation. The temperature control was effected via a PT 100 with control relay. The temperature was kept constant at 90°C over the entire duration of the digestion process. After a duration of reaction of 6.5 hours, the reactor was emptied. The suspension was then filtered via a suction filter. The filter cake was washed with demineralized water so that no mother liquor remained in the filter cake. The filtered mother liquor was further processed to molybdenum compounds according to the known prior art.
The molybdenum content in the dried filter cake was 11%, which corresponded to a molybdenum yield of 98%.

Example 2

Experimental procedure as described in Example 1, NaOH being fed in until a stable pH of 12 was reached. After a duration of reaction of 3.5 h, the molybdenum content in the dried filter cake was 7%, which corresponded to a molybdenum yield of 99%.

Example 3

Experimental procedure as described in Example 1, air being passed in instead of oxygen. After a duration of reaction of 9 h, the molybdenum content in the dried filter cake was 10%, which corresponded to a molybdenum yield of 98%.

Example 4

0.6 litre of demineralized water was introduced into a heatable stainless steel pot having an effective volume of 2 litres and a total volume of 4 litres. 480 g of technical molybdenum oxide having an Mo content of 62% with a proportion of MoO_3 of 60% were added with stirring so that a homogeneous suspension formed. 400 ml of 50% strength NaOH were added to this suspension until a pH of 11 was reached. Air was passed into the stirred reactor via a lateral inlet tube at a volume flow rate of 350 l/h. The air feed was effected directly below the stirring member in order to ensure a good distribution of the small air bubbles in the suspension. The stirring member used was a disc stirrer. The stirring speed was 1000 rpm. In order to avoid concentration changes, the apparatus was operated under reflux. The heating was effected by means of external heating bands. The suspension was heated to 90°C. The temperature control was effected via a PT 100 with control relay. The amount of air was determined via a variable area flow meter (Rotameter). After a duration of reaction of 5 h, the molybdenum content in the dried filter cake was 3%, which corresponded to a molybdenum yield of > 99.5%.

Example 5

0.6 litre of demineralized water was introduced into a heatable stainless steel pot having an effective volume of 2 litres and a total volume of 4 litres. 480 g of technical molybdenum oxide having an Mo content of 62% with a proportion of molybdenum in the form of MoO_3 of 89% were added with stirring so that a homogeneous suspension formed. 50% strength NaOH was added to this suspension with stirring until a pH of 9.5 was established. The suspension was heated to 95°C. Thereafter, 150 g of 30% strength H_2O_2 solution were metered in over a period of 1 h. The pH of 9.5 was kept constant during this time by further addition of NaOH.

The H_2O_2 feed was effected directly below the stirring member in order to ensure good distribution in the suspension. The stirring member used was a disc stirrer. The stirring speed was 1000 rpm. In order to avoid concentration changes, the apparatus was operated under reflux. The heating was effected by means of external heating bands. The temperature control was effected via a PT 100 with control relay. After the duration of reaction of 1 h, the Mo content in the dried filter cake was 7%, which corresponded to an Mo yield of 98%.

Claims

1. Process for digesting sparingly soluble molybdenum oxide concentrates, comprising the following steps:

a) suspending of the molybdenum-containing starting material in an aqueous solution,

b) metering of alkali solution of the alkali metal selected from the group (Na, K, Li) and/or mixtures thereof into the suspension from step a) and establishment of a desired pH with stirring, an oxidizing agent simultaneously being introduced,

d) production of a molybdenum-containing product which contains at least 98% of the molybdenum used.

2. Process according to Claim 1, characterized in that gases from the group consisting of air, oxygen, ozone and/or mixtures thereof are used as oxidizing agents.

3. Process according to Claim 1, characterized in that liquid compounds from the group consisting of hydrogen peroxide, peroxodisulphates of the alkali metals and/or mixtures thereof are used as oxidizing agents.

4. Process according to at least one of Claims 1 to 3, characterized in that the amount of oxidizing agent fed in is at least the stoichiometric amount, based on molybdenum(III) oxide.

5. Process according to at least one of Claims 1 to 3, characterized in that the amount of oxidizing agent fed in is at least the majority of the stoichiometric amount, based on molybdenum(III) oxide.

6. Process according to at least one of Claims 1 to 5, characterized in that the pH of the suspension is at least 8.

7. Process according to at least one of Claims 1 to 5, characterized in that the pH of the suspension is at least 11.

8. Process according to at least one of Claims 1 to 7, characterized in that the

suspension is heated to a temperature of at least 50°C.

9. Process according to at least one of Claims 1 to 7, characterized in that the suspension is heated to a temperature of at least 80°C.

10. Process according to at least one of Claims 1 to 7, characterized in that the suspension is heated to a temperature of at least 90°C.