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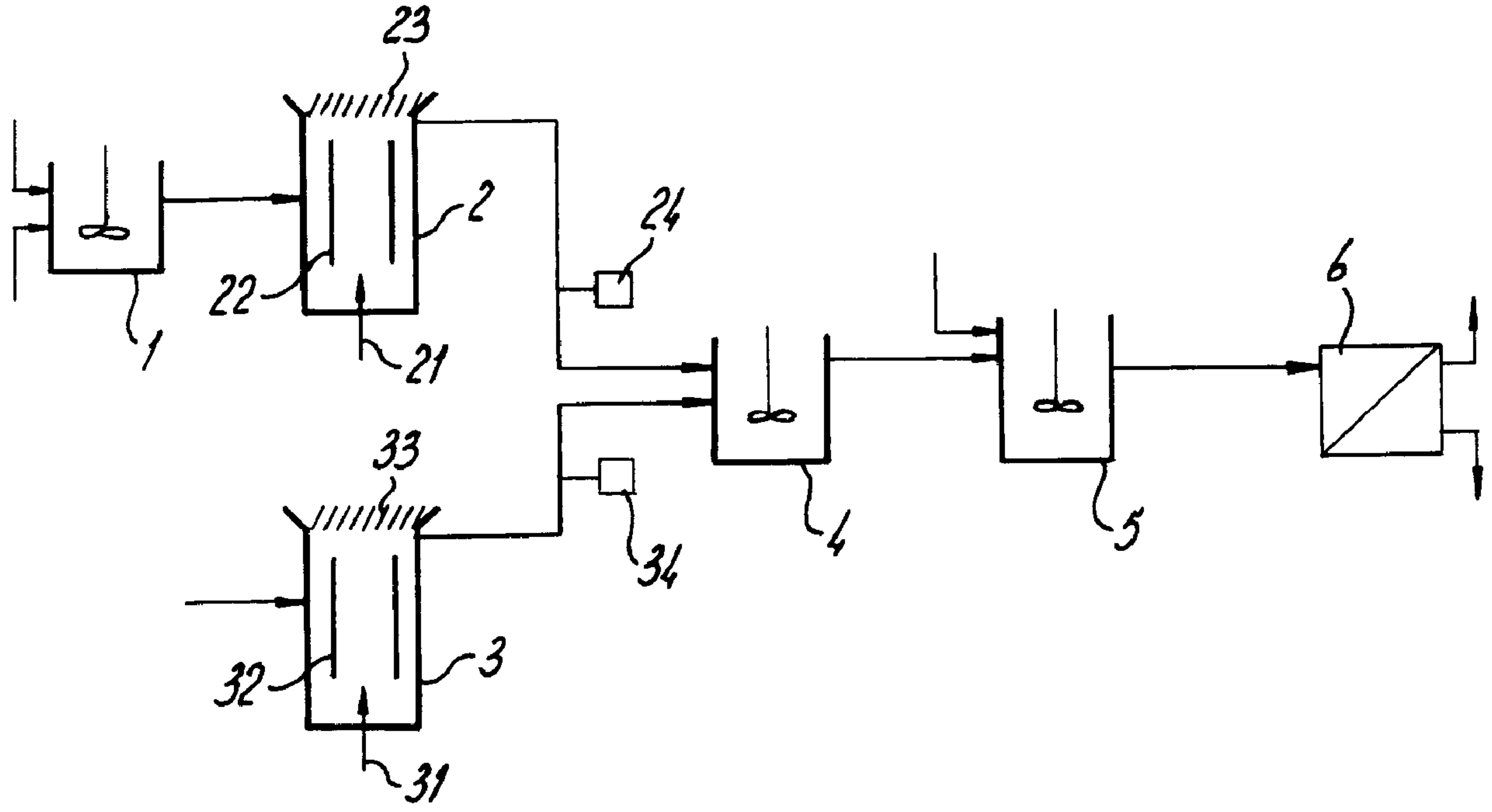
(54) Title: PROCESS FOR IMMOBILISING ARSENIC WASTE



(57) **Abrégé/Abstract**:

The invention provides a process for removing and immobilising arsenic from an arsenic-containing waste. It comprises oxidising the arsenic to pentavalent arsenic in an aqueous medium, contacting the pentavalent arsenic with trivalent iron to form an insoluble iron-arsenic compound and separating precipitated iron-arsenic compound from the aqueous medium. The oxidation of arsenic is effected using oxidising bacteria at a pH between 0.5 and 4 and at a temperature between 20 and 90 °C in the presence of a mineral catalyst such as pyrite.

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(54) Title: PROCESS FOR IMMOBILISING ARSENIC WASTE

(57) Abstract: The invention provides a process for removing and immobilising arsenic from an arsenic-containing waste. It comprises oxidising the arsenic to pentavalent arsenic in an aqueous medium, contacting the pentavalent arsenic with trivalent iron to form an insoluble iron-arsenic compound and separating precipitated iron-arsenic compound from the aqueous medium. The oxidation of arsenic is effected using oxidising bacteria at a pH between 0.5 and 4 and at a temperature between 20 and 90 °C in the presence of a mineral catalyst such as pyrite.

Process for immobilising arsenic waste

[0001] The present invention relates to a process for immobilising arsenic ions comprising oxidising arsenic to pentavalent arsenic and supplying trivalent iron, and subsequently immobilising the pentavalent arsenic as an iron arsenate.

[0002] Arsenic is an important and unwanted by-product in many metallurgical processes. For example, copper ores contain a substantial amount of arsenic, which is undesired for health and environmental reasons and must therefore be separated from the copper metal and be safely disposed of. In pyrometallurgic processes, arsenic is usually separated from off-gas and converted to arsenic trioxide (As_2O_3). This trivalent arsenic compound is unstable, since arsenic is slowly oxidised to pentavalent arsenic. Where there is no use for such arsenic trioxide, it should be carefully deposited so as to avoid leaching of arsenic to the aquatic environment.

[0003] A conventional method for separating and disposing arsenic form metallurgical process streams involves chemical oxidation of the arsenic-containing liquid, which also contains iron, in an oxygenated autoclave at about 90°C at pH 3-4. The pentavalent arsenic thus produced is then converted to a stable insoluble ferric arsenate typically having a molar Fe/As ratio of at least 4 (see e.g. G.B. Harris, *"The Control and Disposal of Arsenic in Hydrometallurgical Systems"*, 24th Annual CIM Hydrometallurgical Conference, Toronto, Ontario, August 20-21, 1994). This chemical oxidation using autoclaves is expensive because of the use of expensive equipment and chemicals, and because of high training costs to avoid personal hazard.

[0004] US 4,888,293 discloses a process wherein a mixture of pyrite and arsenopyrite with a molar Fe/As ratio of about 4:1 is treated with a mixed culture of *Thiobacillus ferrooxidans, T. thiooxidans and Leptospirillum ferrooxidans* resulting in a strongly acidic (pH 1.1) solution. This solution is neutralised and produces a precipitate containing iron arsenate and jarosite, having an Fe/As ratio in the order of 8.

[0005] A new process for the immobilisation of arsenic has been found, involving biological oxidation of arsenic to pentavalent arsenic as well as supply of trivalent iron, in particular by biological oxidation of scrap iron. This oxidation results in effective oxidative solubilisation of the metals followed by effective disposal of the arsenic. The process is defined in the appending claims.

[0006] The oxidation of trivalent arsenic in the presence of iron is carried out using suitable oxidising bacteria. In general, these bacteria assist in the oxidation of divalent iron to trivalent iron using oxygen and acid (protons). Suitable bacteria are usually present in the raw materials (ores) from which the arsenic waste originates. Suitable bacteria can also be derived form other biological, aerobic waste treatment plants. The bacteria capable of oxidising iron and arsenic will normally spontaneously become dominant as a result of the process conditions which can be selected by the skilled person. The bacteria can be heterotrophic such as soil bacteria of the genera *Pseudomonas, Achromobacter, Bacillus* (especially *B. cereus*) and *Alcaligenes* (especially *A. faecalis*). It is preferred, however, that the bacteria are autotrophic bacteria, as these do not need other carbon sources than carbon dioxide, which may be present in sufficient amounts in the waste to be treated, e.g. in the form of carbonates ($FeCO_3$) or with the air supplied to the oxidation process. Suitable autotrophic bacteria for oxidising sulphur and/or iron species include mesophilic bacteria, in particular *Thiobacillus* species such as *T. ferrooxidans* and *T. thiooxidans* and *Leptospirillum* species including *L. ferrooxidans*, moderately thermophilic bacteria, in particular *Acidomicrobium, Sulfobacillus* and *Thiobacillus* species and extremely thermophilic bacteria, in particular *Sulpholobus* and *Acidianus* species such as *S. acidocaldarius*. Mesophiles are typically active at temperatures from about 20°C to about 45°C, moderate thermophiles at about 45 to 65 °C and extreme thermophiles at between about 65 and 90°C.

[0007] The biological oxidation is carried out at a pH between 0.5 and 4, especially between 1 and 3, at a temperature (depending on the type of bacteria used) between ambient temperature and about 85°C or even up to 90°C. A process using mesophilic bacteria is preferably operated at 30 to 45°C, while a process using thermophilic bacteria is preferably performed at 50 to 80°C. Hyperthermophilic bacteria capable of activity between about 75 and 90°C, which can be isolated from hot pools and other hot water sources, can be used according to the invention at those high temperatures. The biological oxidation of arsenic usually requires the presence of a mineral catalyst, in particular a (semi-)noble metal or a metal or metal complex in the galvanic series from noble metals downwards to complexes comparable to pyrite-type minerals. The latter include pyrite, chalcopyrite and molybdenite. The catalyst should have a clean surface.

[0008] The reaction for oxidative arsenic trioxide dissolution by ferric ion can be represented by the following equation:

$$As_2O_3 + 2\ Fe_2(SO_4)_3 + 5\ H_2O \rightarrow 2\ H_3AsO_4 + 4\ FeSO_4 + 2\ H_2SO_4$$

The ferric ion is regenerated by the bacteria using oxygen, so that the net reaction is conversion of As_2O_3 with oxygen and water to H_3AsO_4.

[0009] The trivalent iron necessary for producing the insoluble arsenic compound can be added as such, if an economic source of soluble trivalent iron is available. However, a suitable source of readily soluble trivalent iron is often not available, while a cheap source of iron may be present, especially at a mining site. A common source of iron is pyrite (FeS_2) or pyrrhotite (FeS or Fe_7S_8). Also oxidation products thereof, such as iron oxides, can be used. Most advantageously, the source of iron is iron scrap, which is usually available at mining sites and other sites where arsenic should be disposed, e.g. in the form of broken or unused equipment, rails, scaffolding or the like.

[0010] It is preferred then that the trivalent iron is produced by biological oxidative dissolution of the iron source, using the same bacteria as those assisting in the oxidation of arsenic. The oxidations can be performed simultaneously in the same reactor, but preferably, the generation of trivalent iron in solution is performed in a separate reactor. In the former case, pyrite used for catalysing the arsenic oxidation can be used to provide iron for ferric arsenate precipitation as well.

[0011] The precipitation of arsenic in a stable form occurs with an excess of ferric ion resulting in a stable amorphous ferric arsenate. The stability was found to be satisfactory when the Fe/As molar ratio in the precipitate is greater than 4. For a 10 g/l arsenic solution, the precipitation starts at about pH = 3. The following reaction may occur:

$$2\ H_3AsO_4 + 4\ Fe_2(SO_4)_3 + 22\ H_2O \rightarrow 2\ FeAsO_4.3Fe(OH)_3.2H_2O + 12\ H_2SO_4$$

[0012] The overall reaction produces acid. However, the iron source may contain some acid-consuming gangue. Furthermore, the acid production can be reduced by using iron-bearing minerals with lower sulphur levels. When pyrrhotite is used instead of pyrite, the bio-oxidation of the iron-bearing mineral becomes acid-consuming rather than acid-producing.

[0013] A preferred option according to the invention is to precipitate the arsenic acid under carefully controlled conditions as crystalline scorodite ($FeAsO_4.2H_2O$; Fe/As = 1), which considerably reduces the iron requirement and hence the acid production. This requires a molar ratio of iron to arsenic of about 1:1. Thus, the amount of iron added is adjusted such that this ratio is achieved in the precipitation reactor. Preferably between 0.9 and 1.8 mole of iron is used per mole of arsenic present in the arsenic-containing waste to be treated. The net reaction is than as follows:

$$2\ H_3AsO_4 + Fe_2(SO_4)_3 + 2\ H_2O \rightarrow 2\ FeAsO_4.2H_2O + 3\ H_2SO_4$$

When the iron dissolution is assumed to be the rate-limiting step, the kinetics of the overall process rises considerably when less iron is needed. The oxygen requirement will then go down, bringing down both the operational cost and the capital cost.

[0014] The precipitation of crystalline scorodite is favoured, although not necessary. It can take place at elevated temperatures (above 80°C) and at controlled pH (about 2-3, depending on concentrations). As thermophiles can be used for oxidising both the iron and the arsenic, the invention is also suitable for high-temperature applications.

[0015] The process of the invention can advantageously be carried out in an installation as depicted in the accompanying figure 1. According to this figure, the trivalent arsenic waste (e.g. As_2O_3) and the catalyst (e.g. pyrite) are introduced into a mixing tank 1. Means for adjusting the pH to between e.g. 1 and 3 can also be added to tank 1. The mixed liquid is transferred to airlift reactor 2, having an oxygen inlet 21, means for maintaining a vertical recirculation (cylinder) 22, and a plate separator 23 for separating the treated liquid from biomass. A second aerobic (airlift) reactor 3 is fed with an iron source (e.g. pyrite) and also has an oxygen inlet 31, an internal cylinder 32 and a separator 33. Nutrients, including e.g. phosphate and nitrate, may be added to both aerobic reactors 2 and 3. The effluents from reactor 2 and reactor 3 are conducted to a mixing tank 4. The lines between reactors 2 and 3, respectively, and tank 4 may be provided with a metering system 24 and 34, respectively, e.g. a redox indicator, connected to a flow regulator. The effluent of mixing tank 4 is fed to a precipitation tank 5, in which the pH is adjusted to about 4 (using e.g. $CaCO_3$). Instead of distinct tanks 4 and 5, a single mixing/precipitation tank may be used. The solid/liquid mixture from tank 5 is separated in separator 6. The solid precipitate issued from separator 6 is dewatered further and can be deposited. The liquid issuing form separator 6 can be discharged or can be reused e.g. for adjusting the pH in the process.

[0016] Alternatively, the process of the invention can also be carried out in an installation as depicted in figure 2. Similar parts in figures 1 and 2 are referred to by the same numerals. According to this figure, the trivalent arsenic waste (e.g. dissolved arsenite), the catalyst (e.g. pyrite) and the iron source are introduced into the mixing tank 1. Both the oxidation of arsenic and the oxidative dissolution of iron are performed in airlift reactor 2. The further processing can be as described for the installation of figure 1.

Claims

1. A process for removing and immobilising arsenic from an arsenic-containing waste comprising:
    - (a) oxidising the arsenic to pentavalent arsenic in an aqueous medium using oxidising bacteria at a pH between 0.5 and 4 and at a temperature between 20 and 90°C in the presence of a mineral catalyst;
    - (b) adding to the arsenic between 0.9 and 1.8 mole of iron per mole of arsenic, the iron being trivalent iron or being oxidised to trivalent iron, and allowing said pentavalent arsenic and said trivalent iron to form an insoluble iron-arsenic compound having a molar Fe/As ratio of about 1:1; and
    - (c) separating precipitated iron-arsenic compound from the aqueous medium.

2. The process according to claim 1, in which the iron is oxidised to trivalent iron by oxidative dissolution of an iron source using oxidising bacteria.

3. The process according to claim 2, in which the oxidation of the iron is carried out separately from the oxidation of the arsenic.

4. The process according to claim 2 or 3, in which said iron source comprises pyrite (FeS_2) or pyrrhotite (FeS) or an oxidation product thereof.

5. The process according to any one of claims 1-4, in which said trivalent iron is obtained by oxidation of iron scrap.

6. The process according to any one of claims 1-5, in which about 1 mole of trivalent iron is added per mole of arsenic.

7. The process according to any one of claims 1-6, in which said mineral catalyst is a sulphur-containing catalyst selected from pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and molydenite (MoS_2).

8. The process according to any one of claims 1-7, in which said insoluble iron-arsenic compound is scorodite ($FeAsO_4.2H_2O$).

9. The process according to any one of claims 1-8, in which the oxidation of arsenic is carried out at a temperature between 30 and 45°C.

10. The process according to any one of claims 1-9, in which said oxidising bacteria comprise mesophilic bacteria of the species *Thiobacillus ferrooxidans*, *T. thiooxidans* and/or *Leptospirillum ferrooxidans.*

11. The process according to claims 1-8, in which the oxidation of arsenic is carried out at a temperature between 45 and 65°C.

12. The process according to claim 11, in which said oxidising bacteria comprise thermophilic bacteria of the genera *Acidomicrobium*, *Sulfobacillus* and/or *Thiobacillus*.

13. The process according to any one of claims 1-8, in which the oxidation of arsenic is carried out at a temperature between 65 and 90°C.

14. The process according to claim 13, in which said oxidising bacteria comprise thermophilic bacteria of the genera *Sulpholobus* and/or *Acidianus.*

15. The process according to claim 14, in which said oxidising bacteria comprise thermophilic bacteria of the species *S. acidocaldarius*.

16. The process according to any one of claims 1-11, in which the oxidation of the arsenic is carried out in an air-lift reactor.

fig-1

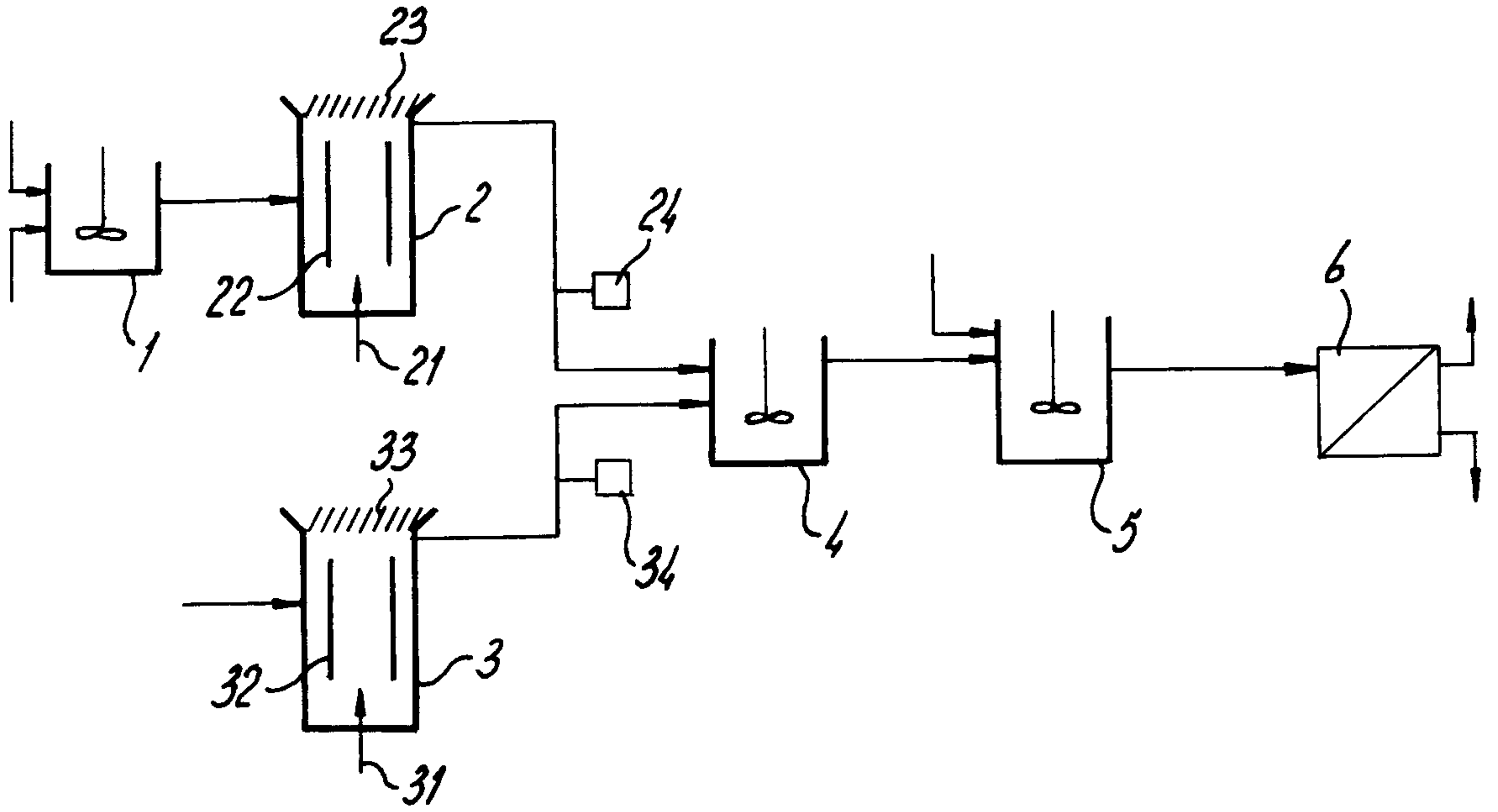
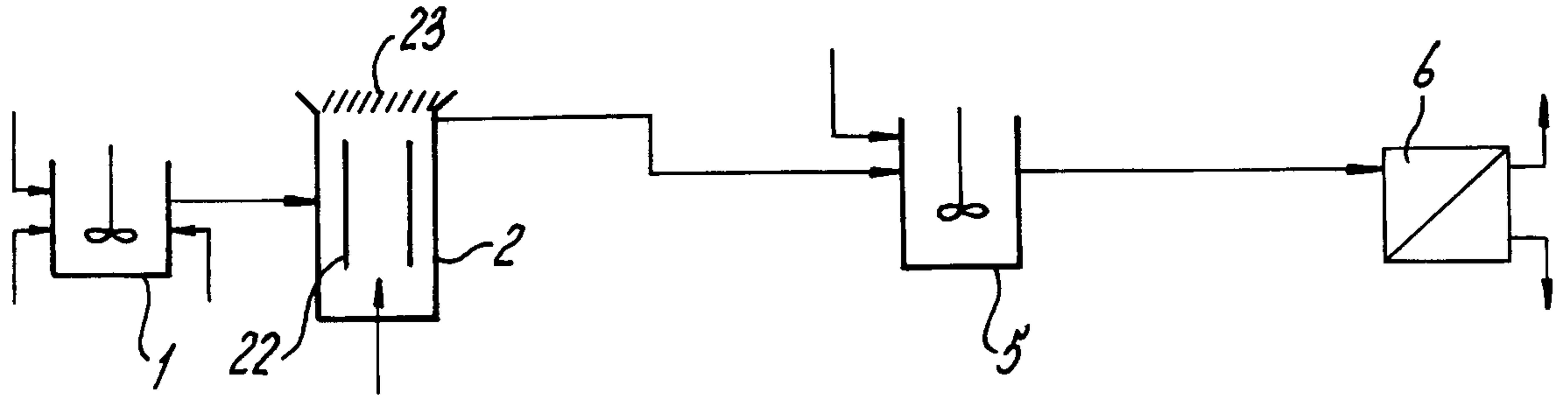


fig-2

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