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(54) Titre : PROCEDE SELECTIF D'EXTRACTION DE MINERAUX DE MINERAIS BRUTS ET APPAREIL POUR LA MISE
EN OEUVRE DU PROCEDE
(54) Title: SELECTIVE PROCESS FOR THE EXTRACTION OF MINERALS FROM CRUDE ORES AND APPARATUS
FOR CARRYING OUT THE PROCESS

(57) **Abrégé/Abstract:**

The present invention relates to a selective process for extracting metals from a raw mineral, which comprises: treating the raw mineral with a dominant microwave magnetic field, or an H-field, in an open-ended single-mode applicator; and separating the products obtained. The process allows continuous operation. To carry out the process, the invention defines a device for processing raw mineral, comprising: a chamber (1) for confining microwaves and selecting H-field mode, E-field mode or alternating E- and H-field mode, according to the complex dielectric permittivity and magnetic permeability properties of the raw mineral; transporting means (7, 8, 9) for transporting by removing the particles of the raw mineral through the chamber; application means for generating a microwave electromagnetic field inside the chamber; and tuning means (4) for tuning and adapting the frequency of the electromagnetic mode.



ABSTRACT

The present invention relates to a selective method of extracting metals from a raw mineral, comprising the treatment of said raw mineral with a dominant magnetic field of microwaves, or H field, in an open single-mode applicator, and the separation of the obtained products. The method allows continuous operation. To carry out the method, the invention defines a raw mineral processing device comprising a chamber (1) for confining microwaves and selecting an H field mode, E field mode or alternating E-H field mode, according to the complex dielectric permittivity and magnetic permeability properties of the raw mineral, transport means (7, 8, 9) for transporting by stirring the particles of the raw mineral through the chamber, application means for generating an electromagnetic field of microwaves inside the chamber, and tuning means (4) for tuning and adapting the electromagnetic mode frequency.

**SELECTIVE PROCESS FOR THE EXTRACTION OF MINERALS FROM CRUDE
ORES AND APPARATUS FOR CARRYING OUT THE PROCESS**

Field of the Invention

5 The present invention is applicable in the field of pyrometallurgical processes of metal extraction, in mining and in recycled materials from the steps of concentration to the step of refining and purification.

Background of the Invention

10 Calcination, roasting, fusion processes are common pyrometallurgical processes for metal extraction. These processes require thermal treatments which allow inducing the mineralogical transformation of metallic ores by means of chemical reactions of decomposition, reduction or oxidation. Pyrometallurgical processes require a high energy requirement because thermal treatments are applied to the combination formed by the ore and gangue mineral and the reactions that take place are not selective
15 enough. Today, thermal treatments are less common in the steps of concentration and enrichment and are often reserved for the more advanced steps of refining and purification, although these treatments are usually complex and costly, they allow obtaining the metal in a higher state of purity.

20 Today, a step with pyrometallurgy methods is often used in the extraction of metals such as iron, nickel, tin, copper, gold or silver. Metallurgical methods such as hydro-, bio-, electro- or pyro-metallurgy do not completely cover the current requirements of metal concentration and transformation in complex polymetallic or monometallic ores with polymineral phases, in low-grade deposits, in rare earth metals, as well as in dump, industrial or electronic waste.

25 The microwave technology applied to minerallurgy emerged as a process of industrial interest in the 1990s. Its interest has increased over time (Bobicki *et al.* "Microwave heating of ultramafic nickel ores and mineralogical effects". Minerals Engineering, 2014, Vol. 58, 22–25). However, its extensive application is still limited, determined particularly by the progresses in the instrumentation, the manufacturing
30 materials, the modelling of microwaves applicators, and by the heterogeneity of the minerals and complexity of the physicochemical interactions occurring with the electromagnetic fields.

 The interactions of the minerals with the electromagnetic fields are based on several phenomena, some of which are still not known properly. In metals, thermal
35 processes with microwaves are linked to the Joule effect (Yoshikawa, "Recent Studies

on Fundamentals and Application of Microwave Processing of Materials. Advances in Induction and Microwave Heating of Mineral and Organic Materials”, S. Grundas, Ed., Croatia, Intech Open Publisher, 2011, pp. 1-26). However, in other mineral components, either original phases or mineral transformation phases formed during treatment with microwaves, other phenomena such as dipolar or ionic phenomenon emerge, in addition to other less known phenomena. Today, there is not enough knowledge explaining all the thermal and non-thermal phenomena generated during treatment with microwaves.

The most widely used microwave equipment in the industry are multi-mode applicators working in the entire electromagnetic field of the microwaves indiscriminately and without selection of the preferred wave propagation path. These multi-mode solutions have a non-homogenous electromagnetic field distribution and a low power density. They do not allow concentrating the energy in specific regions within the applicator, so they have a very limited ability to reach the reaction temperatures in industrial processes. Due to their greater design and operation simplicity, they are more widespread for other applications of lower temperature. In contrast, the single-mode solutions of the microwaves applicators allow concentrating energy with sufficient intensity although, due to their complexity in terms of design and the variables they depend on, the high temperature single-mode applicators are currently limited to discontinuous processes at laboratory scale. Today these applicators focus exclusively on heating with the electric component.

Generally, although microwaves have very a huge potential and relatively high temperatures have been reached in static laboratory equipment, the industrial applications in solids are still very far from the capacity thereof. This is particularly true at temperatures greater than 600°C either because the device is inefficient or because the process is unstable, of heterogeneous treatment and with insufficient control of the reactions taking place. The complexity of the design of the applicators, filters, continuous treatment means and the still limited knowledge concerning the interactions and behavior of the materials with the electromagnetic fields, limit the use thereof.

Dielectric heating is the most common and sought after in microwaves, and the effect of applying the electric field (E field) in the treatment of materials is therefore more well known. The heating induced by means of E field depends on the complex dielectric permittivity of each material and on that of the components thereof, which is typical and furthermore varies with temperature. Dielectric heating is effective for heating a large number of materials (susceptors) but when there is a great difference in

the complex dielectric permittivity of the components forming a compound, such as the case of the presence of high susceptible metals with other very slightly susceptible ones, known phenomena generating hot spots and runaway reactions occur too easily, which complicates or prevents the control of the homogeneous treatments and reactions on most metallic ores and materials containing metals. Such huge differences, which have sometimes been mentioned as a theoretical selective advantage, are a serious drawback which has limited the industrial application thereof and prevented the correct treatment of materials with metallic ores with microwaves effectively.

The effect of the heating induced by the magnetic component of the microwaves (H field) on a material is proportional to the parameter referred to as complex magnetic permeability, which is also typical of each material and varies depending on the temperature. The heating induced by the effect of the H field generates new properties and provides a greater control of the heating in the metals and in the reactions produced. However, applicators for the industry working in the H field dominant for the treatment of metals as proposed in the present invention are not known in the art.

Patent application CN 103447148 relates to a device in which the chemical reduction of the mineral hematites to magnetite is performed by means of heating in a chamber in which microwaves is applied, and which is carried out after a prior heating of the material in a combustion chamber. The chemical transformation of reduction with heating (referred to as roasting) of hematites to magnetite is conventionally used in the industry to allow their magnetic separation from the gangue and recovery as iron ore, but in said application microwave energy is applied as an energy source.

This application is different from the preceding method because it uses a device which by means of an applicator directly carries out a specific exposure to the magnetic component (H field) having the microwave frequency. Specific exposure to the H field allows transformation of the weakly magnetic hematites to magnetic hematites (ferromagnetic) without the need to produce a chemical reduction. Furthermore, when an enrichment or refining is sought, the chemical reactions induced with additives susceptible to a specific field allow the control and applicability of the method in polymetallic ores.

Furthermore, it does not affect the patentability of the invention because this method and devices cannot suggest the application of the present invention as it does not allow the design of the method or the separation of the components of electromagnetic field, it does not allow treatment of other metals besides iron oxides

and less still the treatment of polymetallic ores for extracting their metallic components of commercial interest.

Patent application WO 9808989 A1 describes a desulfurization method through pyrite oxidation with recirculation of the generated gases in a discontinuous process in which microwave energy is used for heating, and in which hematites and sulfur is obtained.

This application is different from the present invention because it describes a treatment process and devices including the non-oxidative decomposition of sulfides, which is not restricted to pyrite, but rather including metallic and polymetallic sulfides, as well as the possible mixtures thereof which can be present, and which to that end requires a specific exposure to the magnetic field (H field) of the microwaves in a single-mode applicator, and which in combination with other successive steps in the E field and E-H allows obtaining commercial metallic components and solid sulfur.

It does not affect the patentability because the method of the application cannot suggest a treatment process and devices because it does not allow the separation of metallic sulfides from different metals, does not allow the extraction and separation of the different metals in polymetallic sulfides and of combinations of other ores and does not allow a continuously industrializable method.

Patent application US4906290 describes a method of treatment of metallic ores for obtaining as a product a precursor for subsequent steps of smelting. The published method uses mineral ores or concentrates mixed with a carbon-containing compound (low level carbons) acting as reducer from a preparation in the form of pellets using microwave energy. The ores can contain oxides or metallic sulfides which once dried by the action of the microwaves will also undergo a general reduction. It uses the known chemical transformation of reduction with heating (referred to as roasting) conventionally used in the industry for concentrating the metal, using microwave energy for heating and initiating the reduction.

This application is different from the present invention because a specific exposure to the magnetic field (H field) is used, in addition to the possibility of exposure to the electric field (E field) in different steps, it allows a highly selective differential heating in only some metallic components and causes transformations of concentrate to levels of elemental metal. The steps of exposure to the specific fields individually allow process control, reaction sequencing and separation of the obtained products.

Furthermore, it does not affect the patentability of the invention because this method cannot suggest the application of the present invention or of the devices

thereof because it does not allow controlling the reactions through treatments with the specific fields of the microwaves, the reduction to elemental metal and the treatment of polymetallic ores for extracting metallic components of commercial interest.

These teachings are not sufficient and are disregarded for continuous
5 treatments with selective and controlled reactions, in processes reproducible at industrial scale in complex low grade polymineral polymetallic and monometallic ores.

Magnetic separation is known and commonly used in mining and industrial processes for concentrating magnetic minerals effectively. However, the process for obtaining a phase with sufficient magnetic properties, from minerals that cannot be
10 magnetically separated (diamagnetic, some paramagnetic), is hard to perform industrially. That is due to the fact that various thermal, electrical, magnetical and chemical phenomena affecting the components of the ores themselves and the reactions thereof with the additions are generated and interact with one another.

The industrial problem to be solved is to be able to attain a continuous,
15 sustainable and profitable, industrializable process which solves the extraction of metals in complex low grade polymineral polymetallic and monometallic ores.

In summary, although potential applications of microwave energy in the processes of minerals in the concentrate of some metals (iron, copper) have been mentioned, an industrial, reliable and robust solution for a large amount of metals is not
20 known today, mainly due to the scaling limitations, efficiency and reproducibility and control of the applied fields, which have prevented the implementation thereof in the industry. The solution proposed by the present invention allows extracting and concentrating the metallic components of commercial interest from polymineral polymetallic or monometallic or low grade ores, at industrial scale and in a continuous
25 process.

Description of the Invention

The present invention is a selective method of extracting metals from a raw mineral, comprising a step of electromagnetic heating of said raw mineral with microwaves in the dominant magnetic field, or H field, in an open single-mode applicator followed by
30 one of the two following options:

- an additional step of dielectric heating with microwaves in the dominant electric field, or E field, and/or a step of dielectric and magnetic heating simultaneously with microwaves in alternating electric and magnetic field, or E-H field, both in a single-mode applicator;

35 or

- an additional step of dielectric and magnetic heating simultaneously with microwaves in alternating electric and magnetic field, or E-H field, and a step of heating with microwaves in the dominant electric field, or E field, both in a single-mode applicator;

5 and separation of the obtained products after each step of heating.

The method preferably allows continuous operation.

In another preferable aspect of the invention, said separation after each step of heating is a magnetic separation of the obtained products, in cold or hot, and as a result of the magnetic properties resulting from the treatment. This separator can also be by
10 Foucault currents or other equivalent means. In another preferable aspect, said separation can be by density.

Extraction of metals is understood as comprising one or more of the associated processes thereof, such as ore concentration, metal enrichment, refining or purification. The raw mineral undergoes therein selective transformation which allows separating and
15 extracting metallic components of higher value generating a new product.

In a preferable aspect of the invention, said raw mineral contains a polymetallic ore and/or a polymineral monometallic ore. In another preferred aspect, this raw mineral is a low grade mineral. In a more preferred aspect, said raw mineral are industrial wastes.

In the scope of the present invention, "raw mineral" is understood as rock, mining
20 byproduct, industrial waste or intermediate product of the treatment susceptible of being processed, containing a metallic ore in addition to the gangue and is previously particulated.

In the scope of the present invention, "ore" or "metallic ore" is understood as the natural or artificial mineral or mineral aggregate containing at least one metal.

25 In the scope of the present invention, "polymetallic ores" is understood as the mineral aggregate containing more than one metal in the constituent minerals.

In the scope of the present invention, "polymineral monometallic ores" is understood as the mineral aggregate containing a metal which is in several mineral phases.

30 In the scope of the present invention, "gangue" is understood as the mineral or mineral aggregate that does not contain metals or has metals in a phase that cannot be taken advantage of economically.

In the scope of the present invention, "extraction of metals" is understood as the process whereby at least one metallic component of commercial interest is obtained from
35 a prior raw mineral of lower value and comprises at least one of the steps of valorization:

concentration, enrichment, refining or purification.

In the scope of the present invention, "concentration" of an ore is understood as the process whereby an increase is achieved in said ore with respect to other ores and to the gangue. This concentration does not necessarily entail mineralogical transformation.

5 In the scope of the present invention, "enrichment" of an ore is understood as the process whereby an increase is achieved in the concentration of at least one of the metallic components thereof which tends to have a transformation process of the mineral itself.

10 In the scope of the present invention, "refining" of ores is understood as the process through which an increase in the concentration of a metal is produced through elimination of impurities.

In the scope of the present invention, "purification" of ores is understood as the process through which an increase in the concentration of a metal up to levels of high metal concentration, which is usually above 85%, is achieved.

15 In the scope of the present invention, "dominant magnetic field" or "H field" refers to that region of the space, in which the relative intensity of the magnetic field of the microwaves represents more than 60% of the total electromagnetic field, such that the mineral receives most of the electromagnetic energy as magnetic energy.

20 In the scope of the present invention, the term "single-mode" refers to the selection of one of the possible solutions of the electromagnetic field in the microwave chamber.

In the scope of the present invention, "microwave applicator" is understood as the part of the system in which the raw mineral is treated, and which is made up of a microwave chamber and the segment of the transport unit going through said chamber. The design of the assembly formed by the microwave chamber and the segment of the transport unit determines the selection to the exposure of H field, E field or E-H field.

25 In the scope of the present invention, "microwave chamber" is understood as the conductive surface structure having a specifically designed internal geometry, confining the electromagnetic field therein and defining the mode of the electromagnetic field.

30 In the scope of the present invention, "single-mode microwave applicator" is understood as that in the microwave chamber of which and by means of tuning, there is only a single mode of the electromagnetic field. A particularity of this applicator is that it is resonant, "resonant" being understood as when the wave of one of the electromagnetic fields is in phase.

35 In the scope of the present invention, "open single-mode microwave applicator" is understood as that having openings wide enough so as to allow the entry and exit of the

raw material and the transport means thereof.

In the scope of the present invention, "dominant electric field" or "E field" refers to that region of the space, in which the intensity of the electric field of the microwaves represents more than 60% of the total electromagnetic field, such that the mineral
5 receives most of the electromagnetic energy as electric energy.

In the scope of the present invention, "alternating electric and magnetic field", or "E-H field" is understood as that region of the space in which the mineral is subjected to a sequence of maximums of H field and E field in an alternating and consecutive manner in single-mode microwave applicator.

10 The additions of susceptible agents acting as reducers, as well as reactive salts and gases in controlled atmospheres allow completing the design of the process for separating the phases of interest. Another preferable aspect of the invention comprises the addition of carbon as reducing component to said particulated ore, prior to any step of treatment with microwaves. Said carbon is very preferably graphite, humates, carbon
15 black, or carbonates. Another preferable aspect is that the method is performed in controlled atmosphere, even more preferable in an anoxic atmosphere in the presence of N₂ or CO₂.

In the scope of the present invention, "controlled atmosphere" is understood as an environment in which the gas composition to which the raw mineral is exposed during
20 treatment in the open single-mode microwave applicator has been modified by means of external provisions of inert gases or with known reactive gases.

In the scope of the present invention, "anoxic atmosphere" is understood as an environment in which the partial oxygen pressure is equivalent to zero.

Sulfur is produced during treatment of the raw mineral with sulfides in an anoxic
25 atmosphere. Another preferable aspect comprises a step of extraction of elemental sulfur by condensation or solidification of the gases extracted from this anoxic atmosphere. To that end, alkaline salts, earth alkaline salts and ammonium salts can be previously added for generating valorizable sulfates and desulfurated metallic components. Therefore, the more preferable aspect comprises an additional step of the direct production of elemental
30 sulfur of high purity by means of a continuous process from cold gases (less than 120°C) extracted from the open single-mode applicator.

Another preferred aspect of the process is the additional application of an external static magnetic field to one or to all the steps of treatment with microwaves. This additional field maintains the magnetization in the mineral and improves the conservation of
35 magnetization resulting from the completion of heating and during cooling until reaching

the Curie or Néel temperature of the metallic mineral component. In minerals less sensitive to the magnetic field, an immediate magnetic separation in a hot condition is carried out. The method can comprise the coupling of magnets or electromagnets that are moved at the end of exit of the applicator and in the cooling area to conserve the resulting magnetization in the mineral.

In another preferable aspect, the raw mineral travels through a container tube having rotational movement. This tube transporting the mineral has a dielectric refractory behavior slightly susceptible to microwaves.

In yet another preferable aspect, the single-mode microwave applicator comprises radiation filters at the ends of the entry and exit. These filters confine the microwaves inside the applicator and prevent leaks.

In the scope of the present invention, "radiation filter" is understood as a device capable of retaining radiation, maintaining the level of leaks within the legal limits, according to the specifications of Directive EC 2004/40.

A highly preferable application of the present invention is a continuous process based on the application of selective electromagnetic fields (E field and H field) or simultaneous alternating field (E-H field) at microwave frequencies between 3 kHz and 300 GHz, corresponding to the so-called ISM (Industrial, Scientific and Medical) bands. In another preferable aspect, the frequency used are that centered in 2.45 GHz, 915 MHz, 433.92 MHz.

The thermal effect of each of the fields produces a selective heating of the mineral reaching high temperature (usually between 300 and 1500°C) and producing therein changes such as decomposition, reduction, oxidation, recrystallization, fusion, etc, as well as others that do not affect the mineral phase, for example changes in the magnetic moments.

Use of electromagnetic field (H field, alternating E-H field and E field) sequencing with a static magnetic field and option of magnetic separation in hot a condition in a continuous device entails the possibility of addressing treatments that were impossible up until now, obtaining a specificity according to the component and allowing the control of the reactions.

The potential of the invention is based on the capacity to perform a selective process, i.e., on the possibility of being able to generate an order of reactions and behaviors affecting the different components in a different and predictable manner, i.e. with the possibility of designing a process. The design of the process is carried out based on the magnetic properties in the microwave frequency (complex magnetic permeability)

and the dielectric properties (complex dielectric permittivity) of the raw mineral and the constituent components thereof conferring polymetallic, polymineral and gangue variability of the raw mineral.

5 In the field of this invention, the energy used for initiating the reactions and for generating changes of properties in the mineral components is provided by the specific exposure to one of the fields of the microwaves. The exposure to the electromagnetic field of the microwaves is carried out in the magnetic field (H field) or in the electric field (E field) or in a system alternating maximums of E field and maximums of H field (E-H field) depending on the phenomenon to be enhanced.

10 By way of example, it can generally be described that the effect of complex magnetic permeability of a component is shown more effectively when it is exposed to H field. Therefore, if the imaginary component of the complex magnetic permeability of a material is high, it suggests a more effective heating (or activation) with the H field, such that those materials having a very low imaginary component undergo a much milder
15 heating (or activation). In a composite material, it is shown that some are heated (or activated) in a different manner that is not the same with the others. This thus also occurs with the complex dielectric permittivity, although with significant differences.

The H field exerts a more selective effect on the raw mineral containing complex ores, so it tends to produce more easily controllable reactions (e.g., with less evidence of
20 unwanted localized overheating phenomena), so many reactions that are not possible in an E field are possible in an H field. The E-H field is also selective for some cases with respect to the E field and H field. The configuration of the process and of the sequence of the steps with specific fields (H field, E field or E-H field) allows predicting and selecting the reactions of interest exclusively on specific minerals.

25 For an effective design, it is convenient to determine the complex dielectric permittivity and magnetic permeability properties of the raw mineral, of the components thereof, and of the reaction products at the temperatures at which they will be treated, for the purpose obtaining behavioral clusters with respect to the H and E fields.

The granulometry of the raw mineral is also a variable. Work has been carried out
30 with material having impalpable fine size (<0.063 mm), but depending on the texture of the grain good results can be obtained with a grain size of several millimeters (<12 mm), and in agglomerate material.

In the present invention, agglomerate material is understood as the particulate material that has been previously treated by means of granulation processes (e.g., pellets,
35 atomized materials).

The products obtained from the different treatment processes applied are differentiable concentrates of the family of antiferromagnetic concentrates (e.g., ilmenite), ferromagnetic concentrates (e.g., magnetite, maghemite, pyrrhotine), ferromagnetic concentrates (e.g., ferromagnetic hematites, Fe, Co, Ni), paramagnetic concentrates (e.g.,
5 paramagnetic wolframite, pyrite, siderite, Al, Pd, hematites), high conductivity diamagnetic concentrates (e.g., Ag, Au, metals of the platinum group), low electric conductivity diamagnetic concentrates (e.g., Pb) and non-conductive diamagnetic concentrates (e.g., quartz, calcite, as well as most of the components forming the gangue).

The most preferable method of the invention comprises the continuous flow of
10 particulate polymineral monometallic or polymetallic ore in the single-mode microwave applicator with the possible additions of reducing agents and reactive salts. The particulate ore flows through a rotating tube coupled according to the longitudinal axis thereof to the single-mode microwave chamber, preferably having a rectangular or circular section working in the frequencies of 2.45 GHz, 915 MHz, or 433.92 MHz. Said ore is
15 exposed to a controlled atmosphere, and elemental sulfur is produced from the generated sulfurated gases by means of the sulfur capture unit. The microwave power applied to the mineral, as well as the temperature reached and the treatment time is controlled in real time by means of impedance sensors, power sensors and temperature sensors, providing the necessary information to be able to operate actuators for tuning and for controlling the
20 flow of the mineral with adjustments in the feeding and rotational speed, inclination and vibration of the tube. The single-mode microwave applicator contains the chamber with a precise internal geometry, which determines the mode of the field and the distribution thereof. The chamber contains a tuning unit incorporated therein adapting the geometry of said chamber for tuning the working frequency in real time. Therefore, the frequency and
25 the mode obtained within the chamber are kept constant within the selected parameters during treatment in view of possible variations, that can occur due to changes in flow rate, composition, temperature or due to the transformations happening in the mineral. This allows controlling and applying the maximums of field in the segment of the transport unit of the applicator through which the raw mineral flows, which will be the H field in some
30 cases, E field and E-H field in other cases. The segment of the transport tube of the applicator is a refractory dielectric slightly susceptible to microwaves. The raw mineral treated in the applicator is exposed to a static magnetic field which is maintained throughout a segment of the cooling area by means of coupled magnet (or electromagnet). A rapid cooling under the static magnetic field favors the maintenance of
35 magnetism in the treated mineral. The filters located at the entry and exit of the applicator

confine the microwave energy in the chamber and prevent leaks. The design of the transformations in the mineral is achieved by combining the type of field with reaction inducers, which are the controlled atmosphere (oxidative, anoxic, reducing atmosphere), the reducing compounds (graphite, humates, carbon black, carbonates) and the additions of reactive salts (alkaline salts, earth alkaline salts and ammonium salts). The magnetic fractions obtained are separated by means of a magnetic separator at low temperatures (<80°C) or in a hot condition, according to the properties of magnetic susceptibility thereof, and the dense fractions are separated by means of a density separator. Each of the treatments characterized by the nature of the mineral, the applied single-mode microwave field, the controlled atmosphere, the reducing additions, the additions of reactive salts and the maintenance of the static magnetic field, defines a step which is before the separation of fractions. The attainment of several steps of treatment configures the process which allows the extraction of metals from complex ores, from which there are extracted byproducts valorizable in intermediate steps of the method (e.g., concentrated ore), in more advanced steps (e.g., new transformants with a high metallic concentration) or final steps with higher degree of purity (e.g., purified metal). An example of same would be that from a wolframite-containing polymetallic a step of concentrating wolframite as recoverable byproduct is obtained, and WO_3 is obtained in a subsequent step of enrichment, and in a subsequent step of purification W would be obtained.

In conclusion, the present invention relates to a metallurgical method and device of extracting metals which is performed in consecutive steps with treatment in one of the modes of one of the components of the electromagnetic field of the microwaves (H field, E field, alternating E-H field) which is applied with high power density of the selected field on the raw mineral and possible additions, and which allows feeding and treatment of the raw mineral in continuous flow. After each step, the separation is performed by means of magnetic separator, and it is complemented in one case with a density separator. Each of these fields acts on the components in a different manner, the H field being more selective than the E field, and cause on the minerals physical and chemical transformation effects alone or by means of additives to encourage precisely the reactions sought.

The selection of the most suitable field is performed according to the complex dielectric permittivity and magnetic permeability properties of the raw mineral, the constituent components, the possible additions and as well as the reaction products. With these parameters, there are obtained clusters of the components which allow identifying the type of field to be applied in the treatment by each step (H field, E field,

E-H field), the necessary additions, and defining the steps for a complete treatment and, ultimately, the process design. The H field is more selective with induction of more controllable reactions and generates magnetization at lower temperatures which is well complemented with steps of processes of E field.

5 The process is industrial by configuration, both in terms of scale and robustness of the treatment itself. It is continuous as a result of using an open single-mode applicator, it is flexible due to its capacity to adapt to the type of raw mineral, it is also modular because it can be carried out with portable devices and it is furthermore a dry treatment. Another significant advantage is that it offers an adaptative control of the
10 process, which is possible as a result of the control system in the single-mode applicators, which makes it more efficient energy wise.

 The process of the present invention can be compatible with other existing processes and offers advantages such as treatment prior to hydrometallurgy treatments, as well as making use of waste which the latter can generate.

15 Therefore, the present invention allows designing each process according to the problem to be solved and allows solving complex mining problems that do not have an effective solution today. It offers supports relevant to the industrial progress, with the availability of processes capable of resolving problems of treatment for extraction of metals in complex ores, such as polymetallic ores, or low grade ores that are not profitable
20 today, or in mineral phases not suitable for other methods, such as sulfides, as well as the capacity of carrying out treatments in raw mineral very rich in metals with microwaves, which had serious limitations today. It furthermore offers solutions to the combination of several of these problems which is enhanced by the capacity of being a highly selective process. Due to the capacity of the different consecutive processes, they can be
25 performed from a concentration of mineral ores extracted from mine even to the extent of applying refining and purification steps.

Brief Description of the Drawings

 Figure 1 shows the graphs of complex dielectric permittivity (dielectric constant and loss factor) measurement tests during the microwave heating.

30 Figure 1a shows the pyrite-rich polymetallic sulfides treated in oxidative atmosphere (air) showing very high values of the dielectric constant and loss factor between 450 and 750°C.

 Figure 1b shows the pyrite-rich polymetallic sulfides treated in inert atmosphere (N₂) showing a very rapid increase in the value of the dielectric constant from 370°C, with
35 a maximum of 16.5 to 430°C and a very sudden decrease at 440°C to 0, recording

negative values in the sensor. The loss factor shows values less than 2.5 up to 400°C, starting from this temperature a sudden increase of the loss factor up to 450°C occurs, recording a value of 38, after which it goes down to values close to 5 in about 650-750°C. The negative data recorded from 450°C of the dielectric constant are associated with a
 5 response of a metallic material.

Figure 1c shows hematite-rich non-magnetic iron oxides treated in inert atmosphere (N₂) having a significant change during heating which is not recovered during cooling. This indicates physical changes (magnetic behavior) which however did not have a mineralogical change associated therewith. This proves the change from paramagnetic
 10 hematites to ferromagnetic hematites.

Description of the legend: Curve with discontinuous line and solid point, dielectric constant (ϵ'); curve with continuous line and empty point, loss factor (ϵ''); curve with symbol x, dielectric constant during cooling after microwave treatment; curve with symbol +, loss factor during cooling.

15 Figure 2 shows the general device of a step.

Figure 3 shows the composite device of a sequence in line with 3 treatment steps.

Figure 4A shows the embodiment of the device with nitrogen injection in raw mineral containing ores with sulfides.

Figure 4B shows a detail of the sulfur recovery unit of a part of Figure 4A.

20 Detailed Description of the Invention

Preferably and in a limiting manner, a system for carrying out the proposed treatment can comprise the following components:

- 1) Feeding unit
- 2) Transport unit
- 25 3) Microwave power generation and distribution unit
- 4) Single-mode microwave applicator
- 5) Tuning unit
- 6) Filters
- 7) Magnet (or electromagnet)
- 30 8) Gas addition unit
- 9) Sulfur capture unit
- 10) Cooling unit
- 11) Control unit
- 12) Separator of treated mineral

35 They are described in greater detail below.

1) The feeding unit is formed by a hopper with a regulable exit for controlling the volume of raw mineral that passes to the transport unit by vibration, or by screw, according to the working flow rate and the granulometry of the mineral. Vibration in the device working at 2.45 GHz was preferred as it has a flow rate greater than 2 kg/h and
5 screw, in that of 915 MHz, as it has flow rates greater than 15 kg/h.

2) The transport unit allows the flow of the raw mineral from the feeding unit through the applicator and the static magnetic field to the exit of the treatment area. It has rotating actuators, inclination variation mechanism and mechanical vibrator in addition to other auxiliary systems, facilitating continuous flow and minimizing accumulations and
10 adhesion of the raw mineral to the walls of the transport element. Said unit is operated by means of the control unit.

The rotational movement in the tube is performed by means of a coupled rotating motor and which is supported on bearings. This movement assures homogenization in transverse section of the raw mineral during treatment in the applicator. Speeds of
15 between 1 and 50 rpm were sufficient for the treated situations.

3) The microwave power generation and distribution unit emits microwaves in a specific frequency band with sufficient power and powers the applicator through a waveguide. It is made up of a power supply source, magnetron head, waveguide and protection elements. The most common working powers, according to the most common
20 performance of current microwave generators themselves in 2.45 GHz are greater than 0.5 kW and up to 12 kW and in 915 MHz are greater than 10 kW and up to 200 kW. In the microwave equipment of 2.45 GHz the WR340 type waveguide with a standard section of 86.36 x 43.18 mm is used. In the frequency of 915 MHz, the WR975 waveguide with a standard section of 247.65 x 123.82 mm is used.

4) The single-mode microwave applicator is the place where the microwave energy is applied to the mineral for treatment. It is made up of two elements: the single-mode microwave chamber and the segment of the transport unit of the applicator, transferring the raw mineral while it is subjected to the microwave energy. It has (inlet and outlet) openings wide enough so as to work in open and allow the continuous flow of mineral.

4.1) The single-mode microwave chamber is constructed by metal having sufficient electric conductivity, durability and thermal resistance (e.g., steel), it has specific design with a precise geometry (preferably having a rectangular or circular section). It houses 2 of the elements of the tuning unit, i.e., the adjustable sliding short-circuit regulating the geometry of the chamber and the adjustable iris.

35 The chamber is protected with very slightly susceptible porous ceramic thermal

insulators and has coupled thereto an external cooling unit.

4.2) The segment of the transport unit of the applicator contained in the microwave chamber which is operated and which allows rotation and vibration. It is formed by a refractory dielectric material slightly susceptible of microwaves. In another configuration a
5 part of the chamber is movable and allows an integral movement with the transport tube.

5) Tuning unit which tunes and adapts the frequency of the electromagnetic mode in said chamber so that it is maintained at the emission frequency of the microwave generator and within a defined interval. Said unit is controlled with the control unit. The main tuning and adaptation elements are: the adjustable sliding short-circuit regulating the
10 geometry of the chamber, the adjustable iris and the impedance coupler for adapting the signal to the raw mineral and maximizing the absorbed energy.

6) The filters are components that are arranged adjacent to the entry and exit of the applicator. They exert a barrier effect against the transmission of the microwaves and prevent the microwave energy from dissipating out of the applicator, which allows the
15 open configuration thereof. They are manufactured from electrically conductive material (e.g., steel, aluminum) and have a specific geometry for each working frequency.

7) Magnet (or electromagnet) for maintaining the resulting magnetization after the action of the microwaves on the raw mineral treated during cooling thereof. It is arranged adjacent to the transport tube in a cooling area and after the applicator, but depending on
20 the desired effect, it is also applied in the terminal part of the applicator. When they are electromagnets, the action thereof is controlled by means of the control unit.

8) The gas addition unit allows incorporating gases within the applicator for working with controlled atmospheres. It has a gas container (cylinder), injector, pressure and flow valves. The injection is performed in the applicator through the transport tube
25 from one of the ends thereof, with control of the gas flow in the flow direction of the raw mineral. Movable windows limit the air openings at the ends of the transport tube for assuring a saturated and controlled environment in the area of the applicator. The working pressures are close to atmospheric pressures.

9) The sulfur capture unit allows obtaining sulfur as recovered valorizable product
30 based on the transformations produced by the microwave treatment in minerals which originally contain S in the form of sulfides. It has an extractor which is coupled at one of the ends of the applicator moving the cold gas (at a temperature less than 120°C) to a heat exchanger in which it is cooled to precipitate same as solid sulfur close to the melting temperature which falls into a tank returning it so that it can be heated to a temperature of
35 120-150°C from which it is poured into the final tanks as elemental S. Gas extraction

elements with SO₂ capturing filters are responsible for preventing risks this gas being released into the atmosphere. The sulfur capture unit is controlled by the control unit.

10) Cooling unit. There is coupled to the end of the exit of the applicator a cooling element for forced cooling by air responsible for cooling the raw mineral below the
5 temperature of change of magnetic properties and maintaining the resulting magnetization within the action of the magnets. It does not work when magnetic separation in hot condition is required.

11) Separator. The device is complemented with a magnetic separator and with a density separator.

10 The magnetic separator performs the magnetic separation operations of the components of the raw mineral according to their properties of magnetic susceptibility. According to the magnetic susceptibility ratios, permanent magnet separator, induced rotor separator, drum separator or even a Foucault separator or a separation in several steps are used. Separation in hot condition is preferred in minerals less sensitive to the
15 static magnetic field.

12) The control unit is responsible for controlling the process of each of the units and integrating same in the process. It has sensors receiving the process information and by means of control logic, through the programmable logic controller, operate the corresponding actuators.

20 To complete the process, sensors are arranged in the entire system: temperature sensors at several points of the process, rotational speed sensors, inclination sensors, mass sensors, magnetic field sensors, pressure sensors, gas flow rate sensors, cooling water flow sensors, electrical power sensors, environmental microwave radiation sensors, magnetic field sensors and other auxiliary sensors.

25 Each family of polymetallic ore or polymetallic monomineral requires a programming conditioned by the sequences of treatments for the designed physical and chemical reactions to occur.

The sensors and actuators forming the control unit are the following:

- Feeding unit controller. It has mass sensors and actuators for operating the hopper
30 outlet, vibration speed (or flow rate in the case of screw).
- Transport unit controller. It has temperature sensors and rotational speed actuator sensors, vibration actuators and inclination actuators.
- Microwave power generation and distribution unit controller. It has temperature
35 sensors for protecting the generator and actuators for variation of the microwave power provided.

- Applicator controller. The process in the applicator requires of specific and characteristic sensors for the impedance and power means, which are very sensitive to mineral changes, which are combined with temperature sensors (pyrometer type), and which by means of the tuning unit allows control adapted in real time. It is made up of the following instrumentation elements:
 - Impedance sensor.
 - Power sensor for sensing microwave power emitted and reflected in real time.
 - Temperature sensors of the contact-probe type and pyrometer type.
 - Actuators of the mechanical components of the real-time tuning unit maintaining the microwave frequency tuned and adapted.
 - Actuators of microwave power.
- Gas injection controller. It has sensors for sensing flow rate, gas pressure, temperature, and actuators for opening and closing gases.
- Sulfur capture controller. It has sensors for sensing pressure in several spots of the circuit, ambient temperature and liquid sulfur temperature, flow rate of gas and liquid, and actuators for cooling circuit and for the heat elements.
- Controller of the cooling unit. It has a sensor for sensing temperature and air flow rate.
- Controller of electromagnet (or magnet) of static magnetic field. In case that the electromagnet is actuated by passing a current.
- Controller of the magnetic separator.
- Controller of the density separator.
- Safety controller. It integrates all the alarm elements of environmental safety, of operation and of occupational safety included in the process and act for correcting or stopping the process in case of identified safety risk. It has sensors adjacent to the ends of the filters (openings of the applicator) with alarms for microwave radiation leak, gas emissions (SO_x, NO_x), residual magnetic fields and electric safety.

The device has been designed to be flexible and modular and allows easy assembling in line according to the complexity of the steps. It also allows a battery arrangement of applicators to be able to reach in the order of hundreds of kilograms per hour.

Hereinafter, in reference to Figures 2-4, several embodiments are described in a

non-limiting manner.

The device for processing in continuous flow of raw mineral containing metallic ores consists of the integration of three fundamental parts: components related with the microwave applicator, components of the transport unit and auxiliary systems, and
5 components of the sulfur capture unit.

Figure 2 shows an embodiment of the device treating metallic ores with microwaves and has an open single-mode microwave applicator (in any of the fields of the scope of the present invention) which is formed by a microwave chamber (1), of rectangular or circular section made of metal with sufficient conductivity, durability and
10 thermal resistance (e.g., steel), plus the segment of the transport tube (7) going through the chamber itself. A microwave generator the wave of which is transmitted by means of a waveguide (3) is coupled to the applicator. The frequency mode inside the chamber (1) is tuned by means of a tuning unit (4). Two filters (2) coupled in respective ends of the microwave chamber (1) prevent the leak of microwaves and prevent the movement of a
15 rotating tube (7) which constitutes the containing and transporting element for the raw mineral. The control unit includes sensors for the impedance and the emitted and reflected power (5) in real time which are coupled to the waveguide.

The process is additionally controlled by means of temperature sensors (6), pyrometers measuring the temperature in the key spots inside and outside the tube, and
20 thermocouples controlling the external temperatures.

The tube (7) is dielectric and is arranged along the applicator. The raw mineral contained in it is thus allowed to move during the treatment, which it does because it turns around its longitudinal axis when it is inclined. A set of bearings fix the tube and allow the rotation thereof operated by means of rotation motors (8) of variable speed which are
25 integrated in a frame (10) which is isolated from the structure by means of "silentblocks". A vibration motor (9) generates the vibration to the transport system mainly used to prevent the compacting inside the raw mineral itself and the adhesion to the tube. The mentioned system for isolating vibrations, "silentblocks", prevents the vibration generated on the rotating tube from being transmitted also to the sensitive parts of the system such as the
30 motors, sensors and microwave generator.

Both the tube (7), the mechanism for rotation and vibration, as well as the components of the microwave applicator are coupled with the frame (10) which allows the precise inclination according to a variable angle (α). The flow rate of the raw mineral is controlled by means of the rotational speed of the tube, the inclination and the vibration. In
35 turn, the forward speed needed for the raw mineral is determined by means of sensors for

sensing mainly impedance, sensors for emitted and reflected power, temperature and flow rate (mass) of raw mineral.

The feeder (11) controls the input flow of the raw mineral.

At the output of the microwave applicator the mineral is separated according to its
5 magnetic properties by means of a separator (12). These properties can be enhanced under hot conditions with an additional static magnetic field (magnet or electromagnet) which is coupled in the external part of the tube and applicator, and which is placed in the final part of the applicator and/or outside same (13).

For the sake of simplicity of the Figure, the cooling unit of the sample and the
10 refrigeration unit of the applicator have not been indicated.

Figure 3 shows an assembly in line of modular devices constituting a cluster of applicators. After a step of treatment, the raw mineral is collected in a subsequent hopper (11B) which can have thermal insulation, which is not usually required in the first hopper (11A), which is introduced in the following applicator module in series. This second
15 applicator module will have a different configuration of electric and magnetic field from that of the previous one and treats the sample in a manner significantly different from the previous one. This step is repeated one or several times with different field configurations and at different temperatures of process until completing the phases of transformation and separation. Each module is independent from the rest with its own rotational speed and
20 inclination (β , γ) according to its rheological behavior. The magnetic separation system (12) can be complemented with an additional density separator, electric property separator, optical property separator, or other type of separator which can be coupled.

The gases produced during the treatment of the raw mineral are collected to valorize them.

Figure 4A shows an embodiment in a controlled anoxic atmosphere which allows
25 preventing the formation of sulfur oxides as a gaseous product. In this process the gas, generally N_2 , is applied through one of the openings of the tube in form of injection which produces a positive pressure and acts by air movement. The collection of the gas is done by suction by means of a capture system (14) for capturing gaseous sulfur which
30 transports the gas to the precipitation system (15), these two systems belong to the sulfur capture unit.

Figure 4B shows in detail part of the embodiment with anoxic atmosphere, in an example with a gas flow in a sense opposite to the raw mineral flow. The capture system (14) has a closing cap (16). The movement of the tube in the applicator is performed by
35 means of a system of bearings, bushes or similar (17). An output conduit (18) removing

gas rich in gaseous sulfur and the input conduit (19) for gas are inserted in this cap, as well as the system for measuring pressure (20). The extracted gas is processed by means of the sulfur capture unit made up of a heat exchanger (21) where the sulfur gases are cooled to give its solid or liquid form and are collected in a tank (23). To make
 5 manipulation easier, it can be maintained in liquid phase during transportation, which is regulated by means of a heating system (24) maintaining the temperature between 120 and 150°C. The exhaust gases are released to the air through a filter (22) of capture or catalysis of SO_x.

Examples

10 In order to describe the present invention in an illustrative but non-limiting manner, the following examples are provided.

In order to design the process the constituent components and the expected resulting components and intermediate phases of the polymineral or polymetallic ore are listed. The relations of complex dielectric permittivity and complex magnetic permeability
 15 are carried out with these components thereby obtaining families of distinguishable behavior, which allows designing the process for modifying the magnetic properties and producing mineralogic transformations allowing obtaining the valorized product.

The samples constituting the raw mineral of each example are common compositions in the nature and in mining waste.

20 The starting samples and the obtained products were studied by means of chemical analysis, with X-ray fluorescence techniques, with inductively coupled plasma for mass spectrometry (ICP-MS) and optical spectrometry (ICP-OES) and microelectronic probe (MEP), and mineralogic analysis by means of X-ray diffraction (XRD), scanning electron microscope (SEM) and petrographic microscope. The results of the analysis of
 25 the examples were reported as% by weight.

The treatments of the following examples were performed with open single-mode applicators with resonant configuration, quartz glass tube with components of ceramic nitride, software-controlled automatic tuning. Feeding was performed with a vibrating feeder coupled with a hopper. In Example 1, feeding was performed with a screw feeder
 30 supported with vibration.

Example 1: Concentration by magnetization in applicator of dominant H field: Case of hematite to magnetic hematite without mineralogical change in iron ores.

A raw mineral containing particulate iron ore having a grain size <0.125 mm with a total iron content of 56% was used. Out of this amount of iron (Fe), 41% is in the form of
 35 hematite, and the rest is in the form of magnetite (FeO·Fe₂O₃), goethite (FeO(OH)) and

siderite (FeCO_3). The rest of the components form the gangue made up of quartz and feldespars.

The raw mineral was continuously processed in a microwave device with a configuration of an open single-mode applicator of H field. The frequency of 915 MHz was used in an applicator of H field of 28 cm in length and 80 mm in diameter, working with a flow rate of 25 kg/h, using a generator with 75 kW of installed power until heating the sample to 690 - 810°C as measured with a pyrometer, measuring from the open end of the exit of the tube. Six magnets of 1.2 Tesla were placed in the end part and up to 60 cm outside the applicator for ensuring that the resulting magnetization was maintained during cooling, which was done with air. The treated raw mineral was passed through a magnetic separator (Frantz model), obtaining a concentrate with a iron content in the form of ferromagnetic hematite higher than 67% and traces of magnetite. The rest of the gangue with a hematite content less than 8% by weight was discarded.

Example 2: Concentration and enrichment of polymineral monometalic iron ore. Decomposition of iron carbonates and magnetization of iron oxides and hydroxides in applicator of E-H field.

A raw mineral formed by an iron ore in several mineral phases ground to grain size less than 0.065 mm, containing iron ores in the form of oxides (hematite), hydroxides (goethite, lepidocrocite: $\text{FeO}(\text{OH})$), hydrated hydroxides (limonite) and carbonates (siderite: FeCO_3) was used. The analytical results performed on the raw mineral based on geochemical and mineralogical analysis showed the following concentration: hematite 53.4%, siderite 26.7%, iron hydroxides and hydrated hydroxides (calculated by difference by weight) make up 8.9%. The gangue is present at 11% by weight in the form of quartz.

A continuous single-mode microwave applicator of 80 cm configured at 2.45 GHz, with simultaneous E and H fields, and with maxima of a fourth of the wavelength between each of the electromagnetic fields was continuously used. The tube was at an inclination of 5°, with vibrating feeder for continuous treatment and turned at a speed of 3 to 4 rpm. The treatment was performed with a flow rate of 3 kg/h using a generator with 3 kW of microwave installed power, until heating the sample to more than 840°C as measured with a pyrometer. Four magnets of 1.2 Tesla were placed in the end part of the applicator, causing the resulting raw mineral to pass through a magnetic separator (Frantz model) still hot between 300 and 150°C, giving the resulting product a Fe content higher than 68.5% in the form of hematite, and with a small magnetite content.

Example 3: Process of enrichment and refining in 2 steps by reduction in complex tungsten polymetallic ores and the presence of other ores (iron, tin) in applicators of H

field and E-H field.

A raw mineral formed by a complex polymetallic ore rich in tungsten and other metals of iron and tin, ground to a grain size of <0.065 mm, containing 40% by weight of wolframite $((\text{Fe,Mn})\text{WO}_4)$, 20% of cassiterite (SnO_2) , 10% of iron oxides (hematite and goethite), and 30% of components of the gangue such as quartz, micas, feldespars and other oxides was used. The hematite was in a predominant form of poorly magnetic hematite (paramagnetic) with a fraction with weak ferromagnetism.

Step 1. Concentration and enrichment in applicator of H field with magnetization of hematite, dehydroxylation of the goethite and separation of wolframite for concentration of tungsten and iron ores.

The raw mineral as a whole was treated in 2 connected applicators of H field. The 2 applicators are connected in line and in direct contact for obtaining the equivalent of an applicator of H field of 24 cm of treatment, each of them having a useful length of 12 cm in length. It was heated to a temperature of $740\text{-}780^\circ\text{C}$ as measured by thermal chamber, setting a magnetic field at the end of the outlet applicator with 4 magnets of 1.2 Tesla. The sample was passed through a magnetic separator (Frantz model) heated between $150\text{-}300^\circ\text{C}$ for obtaining a concentrate in ferromagnetic hematite enriched with $>67\%$ of Fe. The remaining fraction is processed in cold condition in a second drum magnetic separator of magnetic induction and a concentrate was obtained with tungsten oxides by more than 92% after rejecting some mica residues by a blow density method. The rest of the gangue contains amounts of 5% of non-useful iron.

Step 2. Enrichment and refining of tungsten in an applicator of E-H field and reduction of wolframite with potassium humate and graphite for obtaining oxides richer in tungsten

In a second single-mode applicator of E-H field powered with a microwave generator of 3 kW and 80 cm in length, the wolframite was introduced by adding 12% by weight of potassium humate and graphite, having a size less than 0.080 mm. The rotation speed was maintained at 4-5 rpm and with an inclination of 5° to achieve temperatures up to 940°C . The result of the treated samples were tungsten oxides in a more reduced state in the form of WO_3 and W_4O_{11} , as well as potassium humate residues and potassium salts.

The raw mineral was continuously dry processed at the exit with a magnetic separator (Frantz model) for obtaining 2 fractions:

- Fraction having reduced tungsten oxides with an enrichment higher than 92%.
- Remaining fraction (gangue, cassiterite, non-processed wolframite, rests of

potassium compounds).

Example 4: Valorization by aggressive reduction in complex polymetallic tungsten ores, with concentration, enrichment, refining and partial purification

A raw mineral formed by a fraction ground to a grain size of <0.065 mm, containing
 5 40% by weight of wolframite ((Fe,Mn)WO₄), 20% of cassiterite (SnO₂), 10% of iron oxides (hematite and goethite), and 30% of components of the gangue such as quartz, micas, feldespars and other oxides was used. The hematite was in a predominant form of poorly magnetic hematite (paramagnetic) with a fraction with weak ferromagnetism.

Step 1. Concentration and enrichment in applicator of H field.

10 Treatment was performed on the mineral described in Step 1 of Example 3.

Step 2. Applicator of E-H field and reduction of wolframite with graphite, with enrichment and partial purification.

In a second applicator of E-H field powered with a generator of 3 kW and 80 cm in length, the wolframite was introduced by adding 12% by weight of graphite having a size
 15 less than 0.080 mm. The rotation speed was maintained at 4-5 rpm and with an inclination of 5° reaching temperatures up to 940°C. Four magnets of 1.2 Tesla were placed in the end part of the applicator. The obtained result were very reduced phases metal W, concentrated tungsten oxides, in the form of WO₃ and W₄O₁₁ and materials made up of tungsten carbide mainly in the form of Fe₃W₃C being obtained.

20 The resulting mineral, partially compacted after the treatment, was dry ground until obtaining particles of <0.080 mm and was passed through a magnetic separator in dry conditions (Frantz type) in 3 consecutive separation passes, allowing the separation of 4 fractions:

- metal W at 95%,
- 25 - tungsten oxides (WO₃ and W₄O₁₁) at 92%,
- tungsten carbide with iron (Fe₃W₃C) at 98%,
- gangue of non-magnetic minerals and W residues of non-separated phases.

The yields achieved allow suitable industrial balances.

30 Example 5. Treatment of polymetallic sulfides. Extraction of elemental sulfur in applicator of E-H field and E field and enrichment, refining and partial purification of metals

A raw mineral ground to a size less than 0.065 mm and made up of sulfide ores containing pyrite in 85% by weight and other metallic sulfides of Co, Zn and Pb in amounts less than 15% was used. The identified mineral phases were pyrite (FeS₂) as a dominant phase, with minor phases of calcopyrite (CuFeS₂) and traces of pyrrhotite (FeS) and
 35 siderite (FeCO₃).

Step 1. Concentration and enrichment of Fe, Cu, Co, Zn, Pb metals and extraction of elemental sulfur in an applicator of E-H field.

The raw mineral was subjected to a single-mode applicator of E-H field at a frequency of 2.45 GHz. N₂ gas was added by means of direct injection at very low pressure generating a mild flow according to the flow direction of the raw mineral. It was processed at a flow rate of 2 kg/h using a generator with a microwave power of 3 kW which allowed reaching the decomposition temperature up to 750°C as measured with a thermal chamber.

The released gases, with a measured temperature of 118°C, were suctioned maintaining a pressure difference between the processing tube and the suctioning tube close to 10 mbar. The gas was precipitated in the form of solid sulfur by means of cooling in a heat exchanger below 85°C and it was recovered as liquid sulfur of high purity after heating again at 150°C.

The resulting output mineral is formed by iron sulfides of the pyrrhotite-troilite series having a composition Fe_xS (x=1 to 0.8) and other phases containing associated Cu, Ag, Zn and Pb, among which the presence of calcopyrite (around 5% by weight) is identified. The recovered sulfur was 54% by weight of the stoichiometric content of the original pyrite.

Step 2. Addition of Na and Ca salts in an applicator of H field coupled to a second applicator of E field for enrichment, refining and partial purification of Fe and enrichment of other metals

A preparation of chloride and carbonate salts, containing 6% NaCl, 8% Ca₂Cl and 6% CaCO₃ and 4% Na₂CO₃, was added to the mineral obtained in step 1. This compound was then treated in an applicator of H field of 12 cm in length using a rotational speed of 4 rpm to which a second applicator of E field of 12 cm in length was connected, each of which having a microwave generator of 3 kW. Violent reactions are thus avoided. A treatment up to 850°C as measured with a pyrometer was performed.

The mineral was cooled on forced air at a temperature less than 200°C, maintaining a magnetic field of 1.2 Tesla, located in the area closest to the exit of the applicator to maintain a magnetic field and then washed in water for extracting the soluble salts.

The solid residue was passed through a magnetic separator (Frantz type) obtaining two fractions:

- Magnetic fraction: enriched fraction rich in magnetite (FeO·Fe₂O₃) and wüstite (FeO), and fraction of elemental iron (Fe), representing in combination 81% by

weight, in addition to copper oxides, magnetic iron carbides (traces).

- Non-magnetic fraction (weak paramagnetic compounds, diamagnetic compounds): very slightly magnetic fraction with Cu, Ag, Zn and Pb and other minor elements (rare earths), in addition to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Iron carbide components (Fe_xC), known as steels, were also found.

Example 6. Treatment of complex polymetallic sulfides. Extraction of sulfur in an applicator of H field for magnetization, desulfurization and extraction of metallic components

A raw mineral having a grain size less than 0.065 mm rich in copper and iron sulfides and presence of Zn and Pb, in the form of calcopyrite (CuFeS_2), pyrite (FeS_2), spheralite (ZnS) and galena with presence of other minor metallic components (Co, Ni, Cr) and traces (Ag) and non-metallic components (quartzites) was used.

Step 1. Treatment in an applicator of H field for magnetization of sulfides, partial desulfurization and concentration of minerals with Cu-Fe.

The raw mineral was processed in H field, in an applicator with a treatment segment of 12 cm in length, working at a flow rate of solids of 4 kg/h, with a generator with 3 kW of microwave power, with low pressure injection of N_2 gas of industrial quality, reaching a temperature close to 340-430°C as measured with thermal chamber. Four permanent magnets of 1.2 Tesla were placed at the output end to maintain a static magnetic field. The scarce release gases were suctioned maintaining a pressure difference between the processing tube and the suctioning tube close to 10 mbar. The gas was precipitated in the form of solid sulfur by means of cooling in a heat exchanger below 85°C and was recovered as liquid sulfur of high purity after heating again at 150°C. The extracted raw mineral was treated in line with a magnetic separator and a fraction of magnetic sulfides with incipient desulfurization of Cu-Fe and a non-magnetic fraction made up of gangue and the rest of the metallic components were obtained.

Step 2. Treatment of the minerals for enrichment of the metals and production of sulfur in an applicator of E-H field for intense desulfurization of the magnetic fraction

The more magnetic fraction of step 1 and its other associated components (Ni, Co, Cr) was treated in three successive phases with an applicator of E-H field and extraction of sulfur with the same method of step 1, heating to 1050°C, finally giving a fraction of poorly magnetic minerals and enriched in Cu-Fe.

Step 3. Addition of salts of Na and Ca to the non-magnetic fraction in an applicator of H field coupled to a second applicator of E field for enrichment in Fe

A preparation of chloride and carbonate salts, containing 6% NaCl, 8% Ca_2Cl and

6% CaCO_3 and 4% Na_2CO_3 was added to the fraction of raw mineral from step 2.

The composite mixture was then treated in an applicator of H field of 12 cm in length using a rotational speed of 4 rpm to which a second applicator of E field of 12 cm in length was connected, each of which having a microwave generator of 3 kW. Violent
5 reactions were thus avoided. A treatment up to 850°C as measured with a pyrometer was performed.

The mineral was cooled on forced air at a temperature less than 200°C , with 4 magnets of 1.2 Tesla, located in the area close to the exit of the applicator to maintain a magnetic field. It was then washed in water for extracting the soluble salts.

10 The resulting solid fraction was passed through a magnetic separator (Frantz type) obtaining 2 fractions:

- Magnetic fraction: fraction rich in magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) and wüstite (FeO), elemental iron (Fe) representing 79% by weight.
- Non-magnetic fraction (weak paramagnetic compounds, diamagnetic compounds):
15 very slightly magnetic fraction with Ag, in addition to components generated as a reaction byproduct of the sulfides with the salts ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) and the rests of insoluble salts that did not react (CaCO_3). Iron carbide components (Fe_xC) were also found. Separation of the metallic fraction of the gangue (including reaction byproducts) was performed with a density separator under wet conditions.

20 Step 4. Treatment in applicator of E field of the non-magnetic fraction of the step 1 for complete desulfurization and enrichment and refining of Fe, Zn, Pb.

Potassium, sodium and calcium salts (10% CaCO_3 , 6% KCl , 6% NaCl) were added to the non-magnetic fraction of step 1. It was then processed in an applicator of E field of 12 cm in length, reaching temperatures of 890°C . Extraction of the sulfur was performed
25 with the same method as step 1. Iron oxide, zinc oxide, lead oxide, and metallic Zn and Pb, salts as a reaction byproduct and gangue were obtained. All remaining mineral was passed through a density separator under wet conditions for separating the non-metallic components (insoluble salts as a reaction byproduct and gangue) of the metals.

30 Example 7. Extraction of vanadium from alkaline salts in an applicator of H field and E-H field

The starting raw mineral is formed by a fraction ground to a size less than 0.065 mm, containing 65% of iron oxides in the form of hematite (Fe_2O_3) and magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$), in addition to <10% of siderite (FeCO_3) and it contains quartz, feldespars and micas and has a vanadium content of 0.8%.

35 Step 1. Enrichment of Fe in an applicator of H field with addition of graphite and humates

The added components were graphite (5%) and potassium humates (12%) and the combination was treated in an applicator of H field with a flow of 1.1 kg/h using a generator of 3 kW until reaching 790°C. The ends were partially closed in order to generate a high concentration of released gases to facilitate the reduction.

- 5 Once the sample was cooled to 60°C, it was passed through a magnetic separator, obtaining a concentrate of magnetite of 98% in total, with minor contents of wüstite.

Step 2. Enrichment and refining of V in an applicator of E-H field with addition of salts

- 10 6% NaCl and 8% NaCO₃ was added to the raw mineral rich in magnetite from step 1 and this mixture was finally ground, the compound to be processed having a grain size of < 0.045 mm.

Said compound was treated in an applicator of H field to which another applicator of E-H field was connected. Temperature of 850°C was measured in the raw mineral with the treatment in the applicator of H field and temperature of 1150°C was measured in that of E-H field.

- 15 The output mineral was poured directly in water and stirred for 10 min.

The insoluble residue, after drying, gave a concentrate of vanadium oxide of 9.2 g per kg of hematite.

CLAIMS

1. A selective method of extracting metals from a raw mineral, comprising:

- a step of electromagnetic heating of said raw mineral with microwaves in the dominant magnetic field, or H field, followed by an additional step of dielectric heating with microwaves in the dominant electric field, or E field, and a step of dielectric and magnetic heating simultaneously with microwaves in alternating electric and magnetic field, or E-H field;

- a step of electromagnetic heating of said raw mineral with microwaves in the H field, followed by a step of dielectric and magnetic heating simultaneously with microwaves in the E-H field;

or

- a step of electromagnetic heating of said raw mineral with microwaves in the H field, followed by an additional step of dielectric and magnetic heating simultaneously with microwaves in the E-H field and a step of heating with microwaves in the E field;

wherein all electromagnetic fields are applied in an open single-mode applicator, and

separation of the obtained products after each step of heating by magnetic separation of selectively magnetized components, in a dry process of an open rotary system at continuous flow.

2. The method according to claim 1, characterized in that said raw mineral contains a polymetallic or polymineral monometallic ore.

3. The method according to claim 1, characterized in that said raw mineral are industrial wastes.

4. The method according to any one of claims 1 to 3, comprising the addition of carbon as a reducing component to said raw mineral, prior to any step of treatment with microwaves.

5. The method according to claim 4, characterized in that said carbon is graphite, humates, carbon black or carbonates.

6. The method according to any one of claims 1 to 5, comprising the application of an external static magnetic field in at least one step of treatment with microwaves.

7. The method according to any one of claims 1 to 6, which is carried out in the presence of controlled atmosphere.

8. The method according to claim 7, characterized in that said controlled atmosphere is an anoxic atmosphere in the presence of N₂ or CO₂.

9. The method according to claim 10, comprising a step of extracting elemental sulfur by condensation or solidification of the gases extracted from said anoxic atmosphere.

5 10. The method according to any one of claims 1 to 9, characterized in that said single-mode applicator comprises radiation filters in at least one end.

11. A device for the selective extraction of metals from a raw mineral, comprising:
- a microwave chamber (1) configured for confining a single-mode electromagnetic field having a frequency in the microwave range, one of its components, E electric or
10 magnetic H, being dominant or both components being alternating E-H, according to the complex dielectric permittivity and magnetic permeability properties of the raw mineral,
- transport means for transporting by stirring the particles of the raw mineral through the chamber (1) comprising a transport tube (7) and rotation motors (8) capable of stirring the particles,
15 - transmission means configured for transmitting an electromagnetic field having a frequency in the microwave range inside the chamber (1),
- separation means at the exit of the microwave chamber (1) comprising a magnetic separator (12),
- a tuning unit (4) configured for tuning the mode of the electromagnetic field by
20 means of modifying the geometry of the microwave chamber (1).

12. The device according to claim 11, characterized in that the separation means are based on density.

13. The device according to claim 14, characterized in that the transport means are inclinable.

25 14. The device according to claim 11 or 13, characterized in that the transport means comprise a vibration motor (9) for stirring the particles in their movement.

15. The device according to any one of claims 11 to 14, comprising coupled filters (2) to prevent radiation from leaking out when the microwave chamber (1) is open.

30 16. The device according to any one of claims 11 to 15, characterized in that the tuning unit (4) comprises a sliding short-circuit to regulate the geometry of the microwave chamber (1).

17. The device according to any one of claims 11 to 16, characterized in that the microwave chamber (1) has a geometry confining at least one maximum of the magnetic component H of the field in the transport tube (7).

18. The device according to any one of claims 11 to 17, characterized in that the microwave chamber (1) has a geometry confining at least one maximum of the electric component E of the field in the transport tube (7).

5 19. The device according to any one of claims 11 to 18, characterized in that the microwave chamber (1) has a geometry confining the alternating maximums of the components of electromagnetic E-H field in the transport tube (7).

20. The device according to any one of claims 11 to 19, characterized in that the transmission means comprise a waveguide (3).

10 21. The device according to any one of claims 11 to 20, comprising a microwave generator coupled with the transmission means.

22. The device according to claim 21, comprising a control unit configured for controlling the transport means, the transmission means and the tuning unit.

15 23. The device according to claim 22, characterized in that the control unit is configured for equalizing the mode frequency in the microwave chamber (1) to the frequency of the microwave generator.

24. The device according to claim 23, comprising at least one impedance sensor (5), temperature sensor or power sensor.

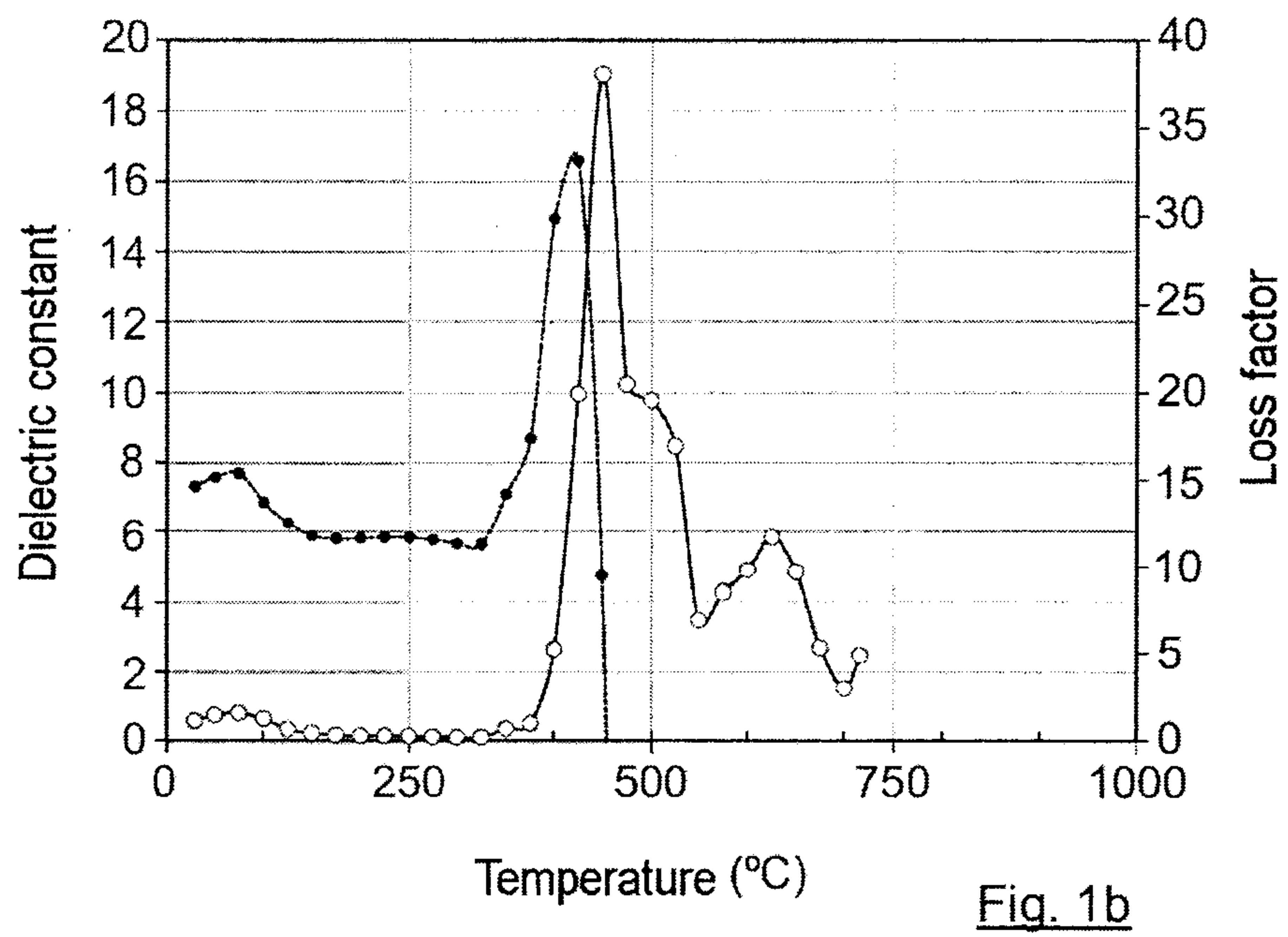
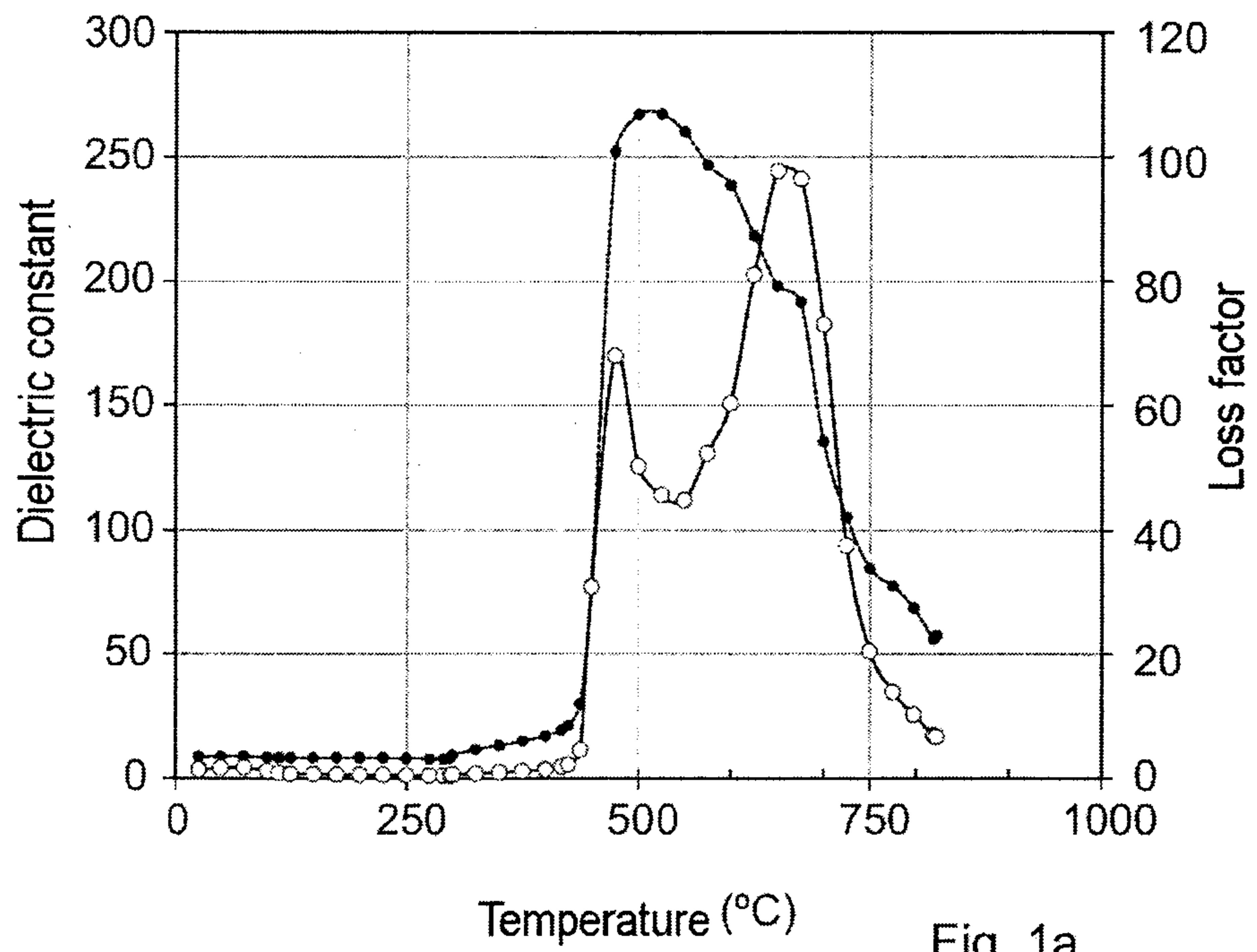
25. The device according to any one of claims 11 to 24, comprising gas addition means for incorporating gases inside the transport tube (7).

20 26. The device according to any one of claims 11 to 25, comprising sulfur capture means for recovering sulfur from the processing by means of an extractor coupled to one of the ends of the transport tube (7).

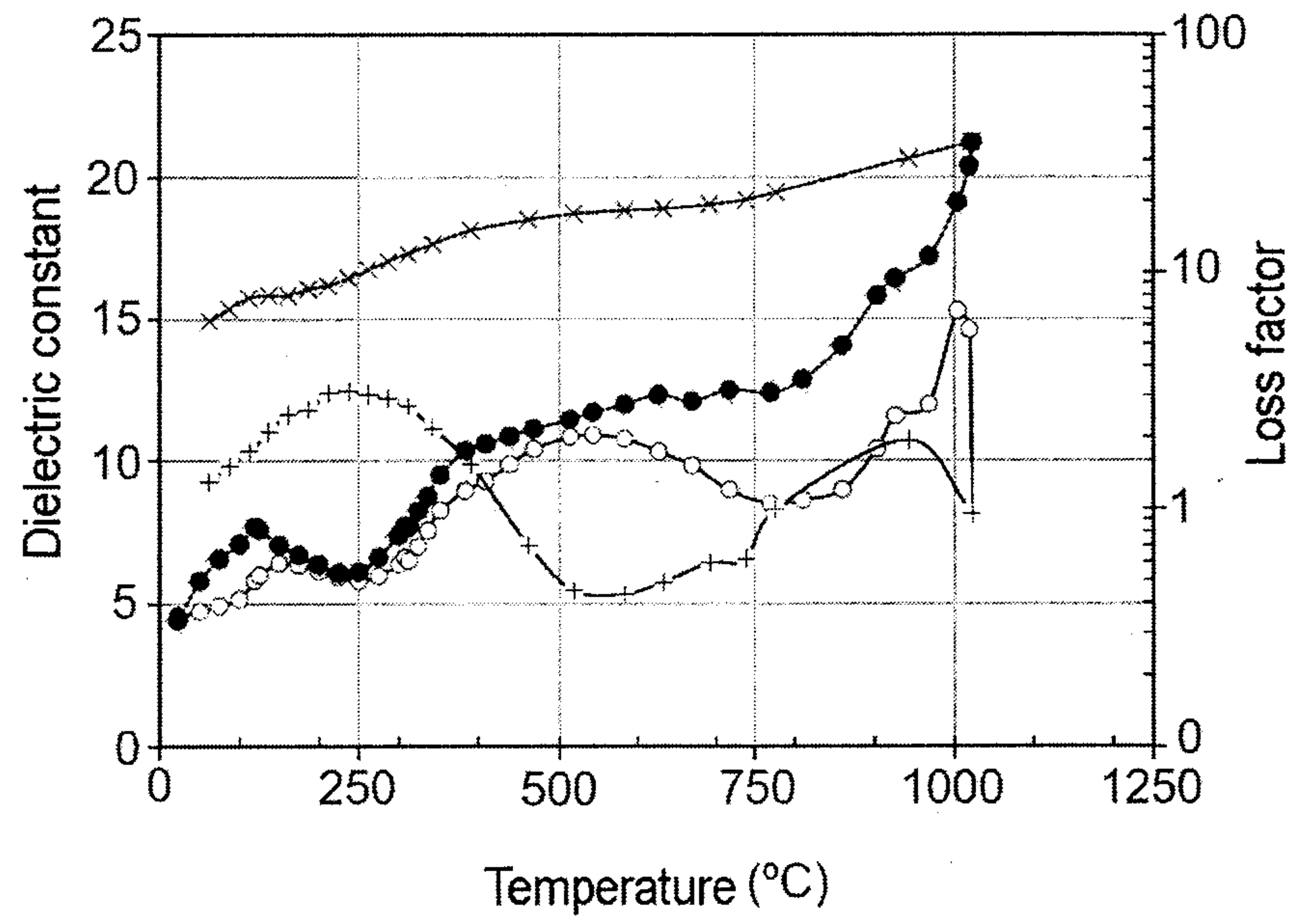
25 27. The device according to any one of claims 11 to 26, comprising a magnet or electromagnet (13) at the exit of the chamber or in the final segment thereof, to maintain the magnetization resulting from the raw mineral treated during cooling thereof.

28. A system for the selective extraction of metals from a raw mineral, comprising a plurality of devices according to any one of claims 11 to 27, arranged in series to sequentially treat in each device at least one component of the raw mineral.

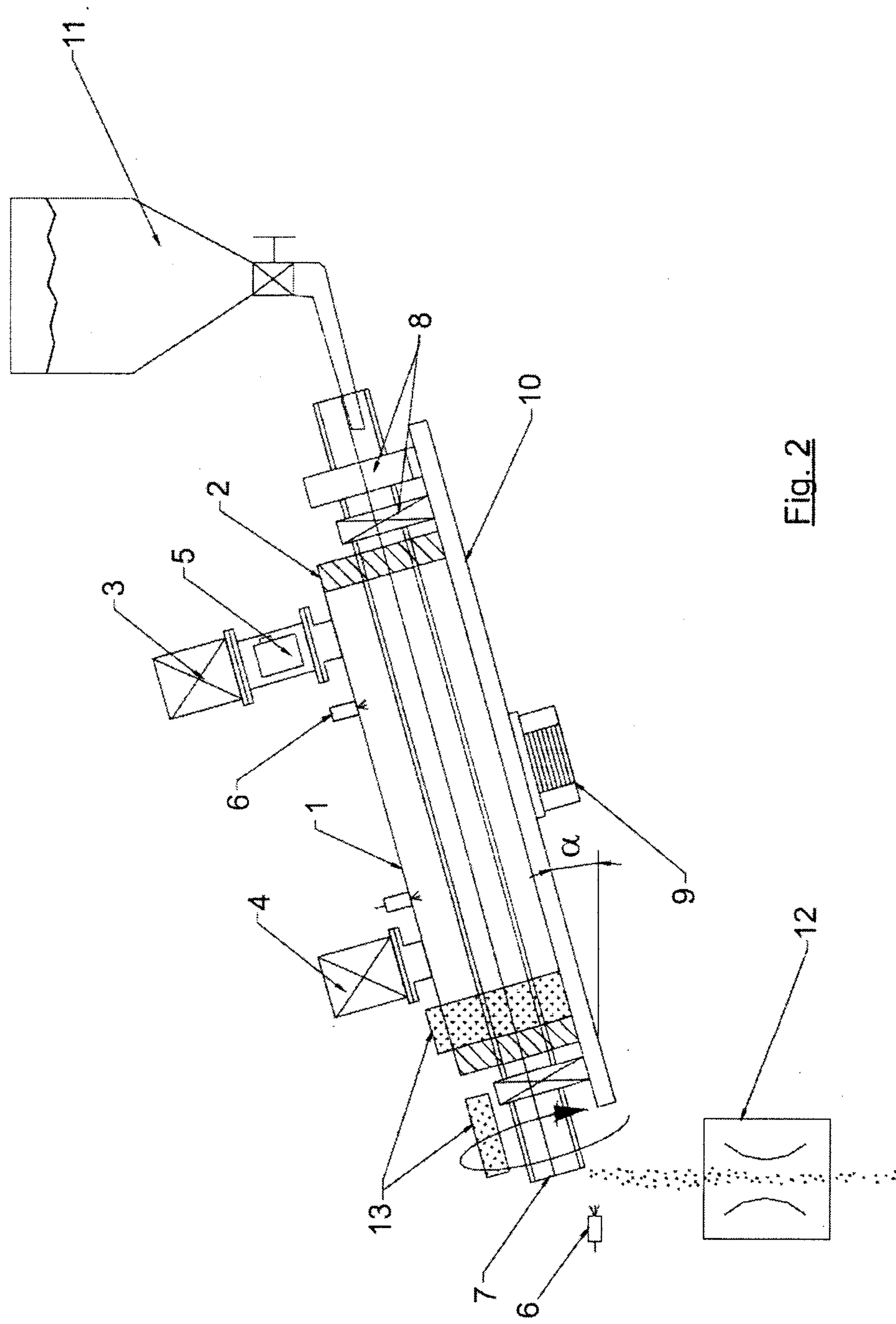
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Fig. 1c

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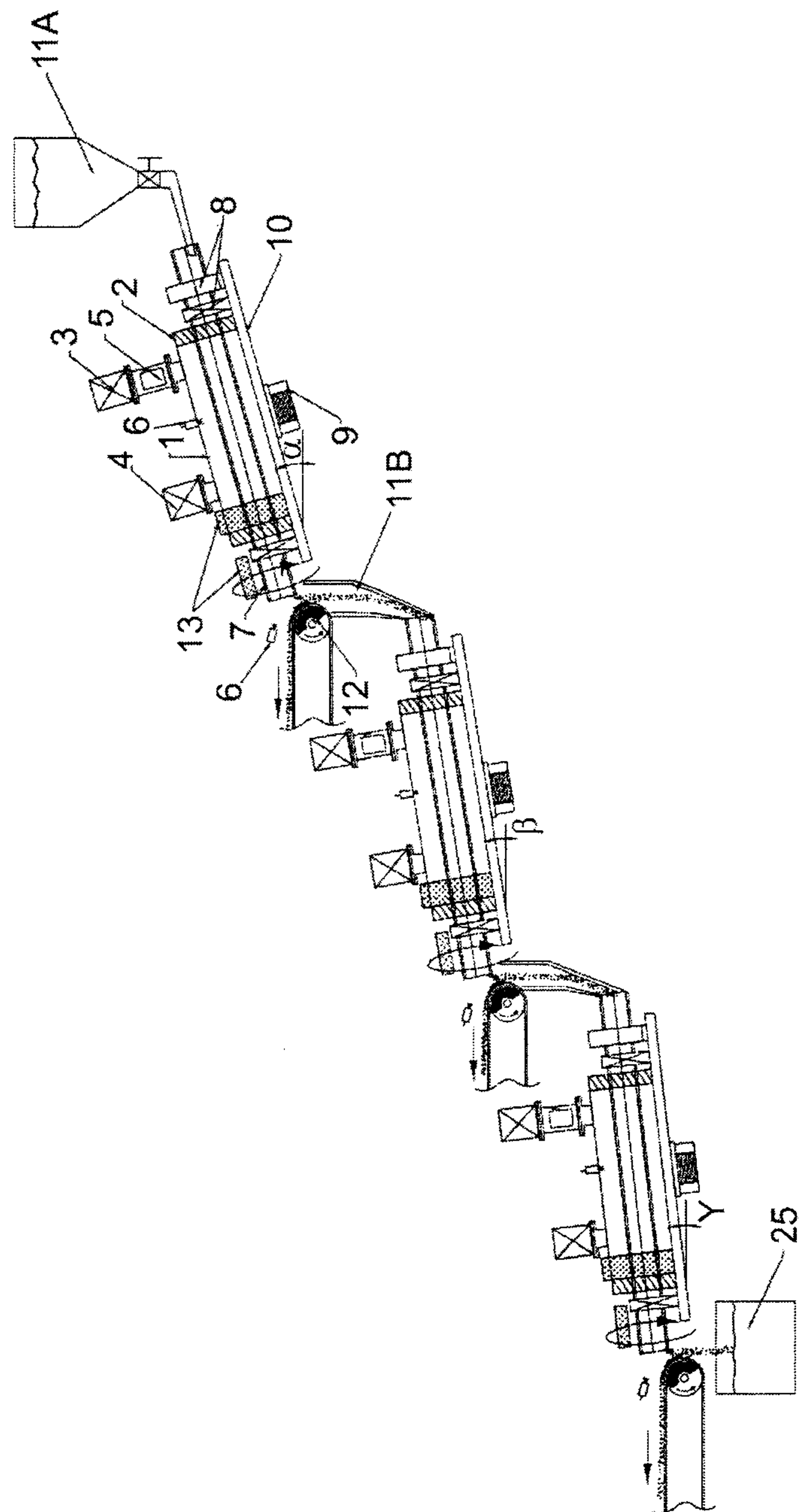


Fig. 3

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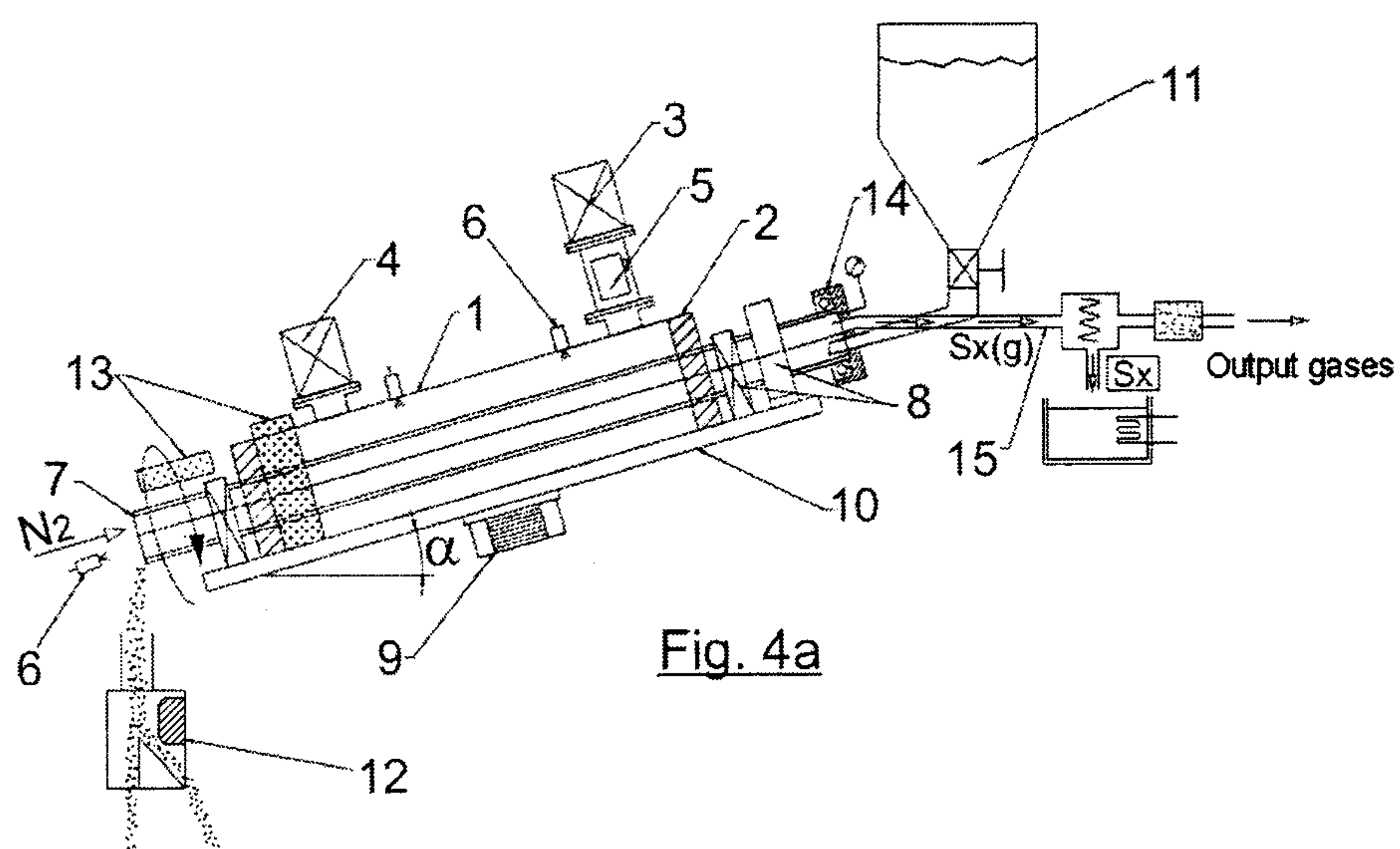


Fig. 4a

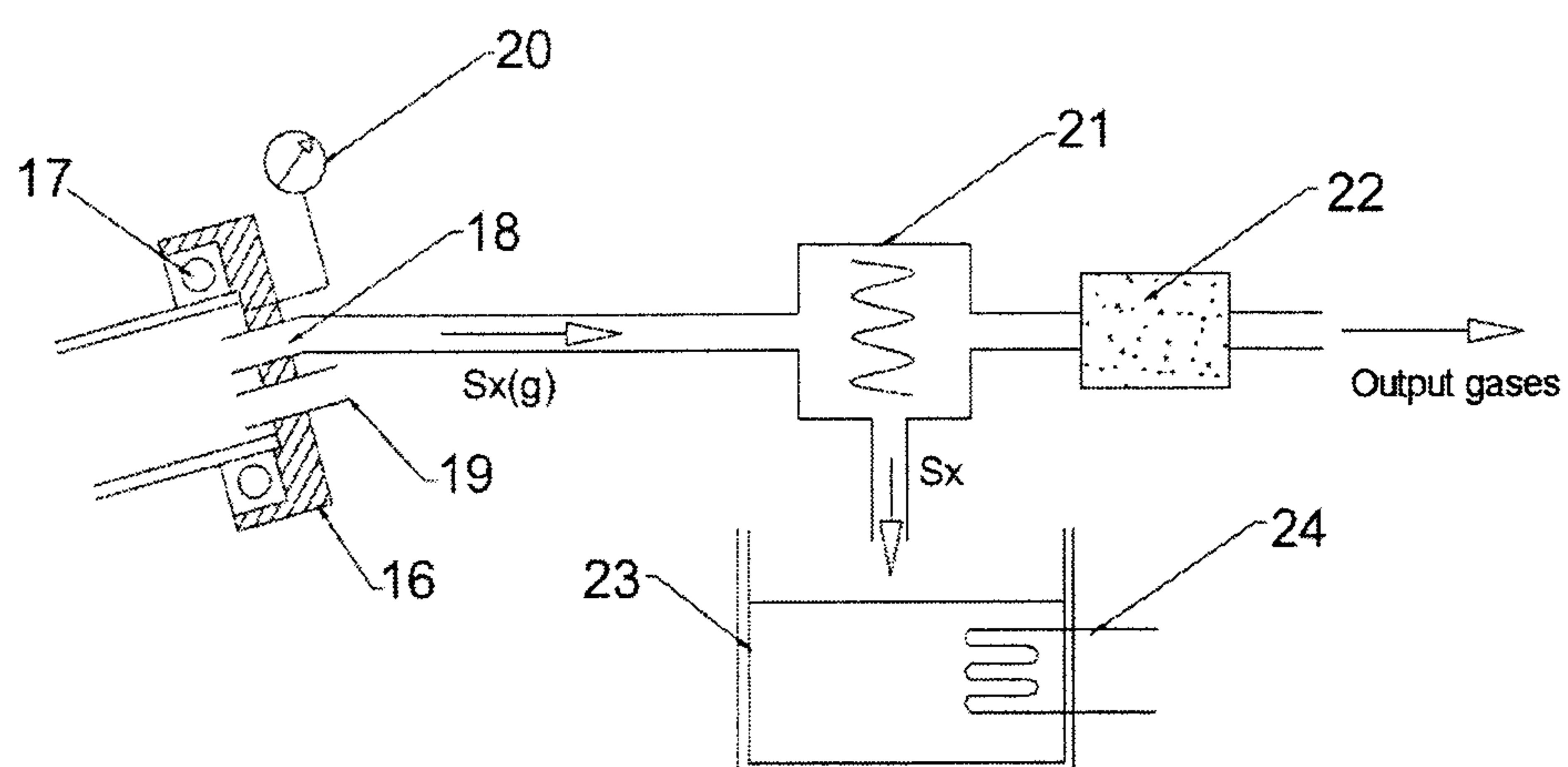


Fig. 4b