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(54) Title: METHOD OF ELIMINATING ODOUR FROM A LIQUID HAVING ORGANIC CONTENT

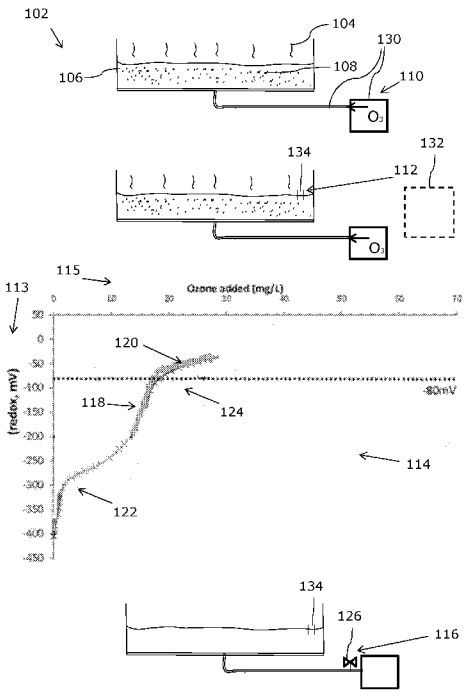


FIG.1

(57) Abstract: In order, e.g., to provide a method of and system for treating various types of liquid having organic content, such as various types of animal manure, in a manner which provides a stable and sturdy result, also when certain conditions changes or varies, there is disclosed a method (102) of controlling an amount of odour(104)from a liquid(106) having organic content comprising adding (110) an oxidising agent, such as air and/or ozone,to the liquid in order to reduce or eliminate its odour, and monitoring a level(112)of oxidation of the liquid, and monitoring a slope (114) of change in the level of oxidation of the liquid, and stopping adding (116) oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit in response to the slope of change of the level of oxidation and at least one criterion correlated to the slope.

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METHOD OF ELIMINATING ODOUR FROM A LIQUID HAVING ORGANIC CONTENT

FIELD OF THE INVENTION

The invention relates to a method of and apparatus for eliminating odour from a liquid, such as animal manure or waste-water, and in particular to controlling an amount of odour from the liquid using an oxidising agent and a feedback mechanism, which will be described further in the following.

BACKGROUND OF THE INVENTION

In a reference method of treatment of a substance having organic content, a method and system is disclosed in which one or more method steps of the treatment may be controlled with a feed back mechanism which is regulated by at least one of the parameters: an optical transmission of the substance, an optical colour of the substance, level of pH, a level of oxidation agent (preferably ozone, O_3), and a level of hydrogen sulphide, H_2S.

Similar reference methods and systems may be seen to have as a disadvantage that treatment of the substance or liquid is quite costly and/or inefficient. The inefficiency may be seen to lie therein that in order to aim for and possibly reach a precise and efficient control of the treatment, possibly rather complex systems and methods are used.

Despite efforts and complexity, at least some reference methods and systems may also or additionally be seen to provide solutions which may be found efficient and well working under certain conditions whereas under other conditions such methods and systems does not seem to be controllable to an extent which may be found sufficient, i.e. some reference methods and systems may be found to have as a disadvantage that a stability of a controllability of the systems is insufficient.

A reason for a disadvantage such as the instability of some reference systems and methods may lie therein that a simple and efficient best mode of controlling such treatment does not yet seem to have been disclosed.

Thus, the applicant for and the inventor of the present invention has appreciated that an improved method of and apparatus for controlling an amount of odour

from a liquid having an organic content is of benefit, and has in consequence devised the present invention.

SUMMARY OF THE INVENTION

It may be seen as an object of the present invention to provide an improved method of and apparatus for controlling an amount of odour from a liquid having organic content. Preferably, the invention alleviates, mitigates or eliminates one or more of the above or other disadvantages singly or in any combination.

Alternatively or additionally, it may be seen as an object of the invention to provide a method of and system for controlling the amount of odour in a manner which provides a stable and sturdy result, also when certain conditions changes or varies.

In particular it may, alternatively or additionally, be seen as an object of the invention to provide a method of and system for treating various types of liquid having organic content, such as various types of liquids having organic content and such as various types of animal manure, while still being efficient, stable and sturdy.

Accordingly there is provided, in accordance with the method aspect of the invention, a method of controlling an amount of odour from a liquid having organic content, such as animal manure, slurry or waste water, where the method comprises adding an oxidising agent, such as air and/or ozone, to the liquid in order to reduce or eliminate its odour, and wherein the method further comprises

- monitoring a level of oxidation of the liquid, and
- monitoring a slope of change in the level of oxidation of the liquid, and
- stopping adding oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit in response to the slope of change of the level of oxidation and at least one criterion correlated to said slope.

Thus, an improved method of controlling an amount of odour from a liquid having an organic content is provided. The odour originates at least partly from hydrogen sulphide in the liquid. The level of odour may be correlated to or express as a function of hydrogen sulphide in the liquid. The improvement or advantage may be seen to lie therein that when applying a method in accordance with what is

described herein, a method is provided which is stable and sturdy and thus efficient when treating various types of liquid having organic content, such as various types of liquids having organic content and such as various types of animal manure.

An improvement or advantage of the present method may be seen to lie therein that in accordance with the method an amount of odour from the liquid is controllable in a sturdy and stable manner in response to a simple measurement of the level of oxidation of the liquid, not the level of pH and/or colour of the liquid etc.

In particular, it may be seen as an advantage of the method that oxidising agent is used efficiently and to an extent as low as possible while the odour is still eliminated. If the oxidising agent is ozone this is of some importance in that an ozone generator and/or maintenance of the ozone generator may be seen to be relative costly. This is particularly important if an ozone generator is needed which generator must be able to provide relative high amounts of ozone. If the oxidising agent is air, then a relatively lower amount of air is needed in accordance with the present method.

The level of oxidation of the liquid may be determined as a function of time. The method may include monitoring a slope of change in the level of oxidation or redox potential of the liquid over time.

Still further and also in particular, it may be seen that the efficiency of the method is provided by monitoring the slope of change of the level of oxidation and stopping or reducing addition of oxidising agent in response to the slope and at least one criterion correlated to the slope of change of the level of oxidation. The slope may be defined using numerical methods or as a differential coefficient determined at the point of interest. The slope of change may be measured over an interval, e.g. over a specific period of time. Hereby it has been found that a method for eliminating or reducing the odour of the liquid is provided which is stable and sturdy for various types of liquids having organic content and in particular for various types of animal manure.

In accordance with preferred embodiments of the method the at least one criterion correlated to the slope of change of the level of oxidation comprises

either criterion a) or b). Thus, stopping adding oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit when or just after

a) at a level of oxidation of more than a predetermined level, such as minus 200 mV, said slope of change decreases from a relatively high first level to a relatively low second level or when or just after
b) at any level of oxidation, said slope of change changes from the relatively high first level to a relatively low second level for a second time.

In that the oxidation level of certain liquids, such as animal manure, may decrease again rather rapidly, such as decrease 5 mV during a period of 24 hours, addition of oxidising agent may not be stopped or completely stopped when the slope changes as described, but a minor amount of additional oxidising agent may additionally be added in order to give the liquid a certain odour free storage period. Alternatively, only a reduced amount of oxidising agent sufficient to maintain an odour free oxidation level is added per time unit.

When or just after is understood as either when or just after having added a certain amount of oxidising agent or when or just after having reached a certain level of oxidation level or at a certain moment of time.

It has been found that the level of oxidation, when stopping adding oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit, and thus when having eliminated or significantly reduced the odour from the liquid is in an interval from and including minus 150 mV to and including minus 25 mV, such as about minus 80 mV. For the six different animal manure samples embodied as different types of liquids herein, the level of oxidation when the odour is eliminated is approximately -25 mV, -40 mV, -50 mV, -75 mV, -80 mV and -100 mV, respectively.

At these levels of oxidation, which are all less than -200 mV, the level of change of the oxidation level, i.e. the slope of the oxidation level as a function of the amount of oxidising agent added to the liquid, has changed from the relatively high first level of the slope to the relatively low level of the slope. It has been found that in order for the high/low slope criterion to work efficiently, when ozone is the oxidising agent, the high slope is more than and including 25 mV per mg. ozone added per volume unit of the liquid and the relatively low second level of

the slope is less than and including 10 mV per mg. ozone added per volume unit of the liquid.

Similarly, other tests have shown that the relatively high/low criterion is efficient independent of the type of oxidising agent when stopping or reducing addition of oxidising agent is provided when a ratio between said relatively high first level and said relatively low second level is equal to or more than 25 divided by 10. The oxidising agents may be in solid or fluid form and may e.g. be ozone, oxygen, potassium permanganate, hydrogen peroxide etc.

When the oxidising agent is ozone and possibly when addition of ozone is provided in increments, initially, only about 0.5 to 4 mg ozone may be added per litre of the liquid. In this way it may be assured that not too much ozone is used in order to eliminate the odour from the liquid. In particular it has been found that certain types of animal manure, such as sample '202' herein, only requires about 6 or 7 mg. ozone per litre manure in order to eliminate its malodour. Thus, in order to be able to react to changes in the slope in the level of oxidation, a flow or addition of oxidising agent may be adapted to be provided in increments, such as increments of below three, two or one mg. ozone per litre liquid. Additionally or alternatively, the rate of oxidising agent added per time unit is adapted in order to be able to react to eliminate the odour without adding to much oxidising agent. Alternatively or additionally oxidising agent may continually be added to the liquid until, e.g., addition of oxidising agent is stopped or reduced.

When the type of liquid is animal manure it has been found that addition of about 5 mg ozone per litre of the liquid to and including about 27 mg ozone per litre of the manure, is enough to eliminate the odour of various types of animal manure, but that the amount needed is e.g. conditioned by the exact type of animal manure. In that even a type of manure, such as manure from pigs may vary in dependence of various conditions and factors such as storage time of the manure and/or age of the animals and/or fodder type used for the animals etc., it is important to have a method and system which is able to eliminate odour not only from pig manure but also from other types of manure, so that continued and possibly manual adjustment of the process and/or equipment is prevented.

Similarly it has been found that for a liquid such as waste water, less ozone, such as around 0.5 mg per litre suffices in order to eliminate its odour. Still further, and

possibly more importantly, it has been found that independent of the type of liquid, stopping addition of oxidising agent as described herein assures that the odour is eliminated without using an unnecessary high amount of oxidising agent, thus a precise addition of oxidation agent in order to precisely control emission of odour, measured as emission of hydrogen sulphide, is achieved.

Herein, it is to be understood that preferably, the odour from the manure is considered reduced or eliminated when an emission measured in a number of parts per million of hydrogen sulphide from the liquid is below 0.1 or possibly 0.05 parts per million.

In that, e.g., the level of oxidation may decrease over time, such as if the liquid is stored, the method may further comprise starting or restarting adding oxidising agent to the liquid or increasing addition of oxidising agent to the liquid per time unit in response to the oxidation level. This may e.g. follow when or just prior to when the oxidation level decreases to a level below the level where the odour is eliminated or prevented and thus substantially at a level or just above a level of oxidation where addition of oxidising agent was stopped initially in a first treatment of the liquid. This may be preferred, e.g. when compared to addition of an immense amount of oxidation agent initially, preventing odour but requiring costly equipment and/or costly maintenance thereof.

When compared to the present method, e.g., only 25 mg ozone per litre liquid may be added initially and 5-10 mg/l added later, which has been found enough to prevent the liquid from smelling, including when used, in comparison to a another method of e.g. initially adding 100 mg ozone per litre (thus 75 mg too much) and still having a smelling liquid one week after.

In accordance with an apparatus aspect of the invention there is provided an apparatus for controlling an amount of odour from a liquid having organic content, such as animal manure, slurry or waste water, where the apparatus comprises

- a receptacle for the liquid,
- a system for adding an oxidising agent, such as air and/or ozone, to the liquid
- a control system with a feed back mechanism, and wherein the control system comprises
    - an oxidation level sensor adapted to sense a level of oxidation of the liquid in the receptacle

- an oxidising agent sensor adapted to sense an amount and/or a rate of oxidising agent added to the liquid in the receptacle
- a means, such as a valve, for controlling an amount and/or rate of oxidising agent to be added to the liquid in the receptacle and wherein the control system is adapted to control an amount and/or rate of oxidising agent to be added to the liquid in the receptacle in order to control the amount of odour from the liquid by being adapted to monitor a level of oxidation of the liquid in the receptacle with said oxidation level sensor and by being adapted to monitor the amount of oxidising agent added to the receptacle with said oxidising agent sensor and by being adapted to stop adding oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit with said means, such as a valve, in response to a slope of change of the level of oxidation and at least one criterion correlated to said slope.

The at least one criterion may comprises criterion a) or b) described herein.

Thus an improved apparatus for controlling an amount of odour from a liquid having organic content is provided. In particular it may be seen that an apparatus which provides a stable and efficient elimination of odour from the liquid is provided while only using simple means.

It must be understood that an advantage described herein can be seen as a possible advantage provided by the invention, but it may also be understood that the invention is particularly, but not exclusively, advantageous for obtaining the described advantage. In general the various aspects and advantages of the invention may be combined and coupled in any way possible within the scope of the invention. These and other aspects, features and/or advantages of the invention will be apparent from and elucidated with reference to the embodiments described hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will be described, by way of example only, with reference to the drawings, in which

FIG. 1 is an illustration of a method and system in accordance with an embodiment of the invention,

FIG. 2 is a graph showing an oxidation level in mV. of six different samples of liquid as a function of an amount of oxidising agent added to the liquid in mg./l.,

FIG. 3 is a graph of at least part of the curve showing the oxidation level in mV. of one sample of liquid as a function of an amount of oxidising agent added to the liquid in mg./l.,

FIG. 4 is a graph showing the oxidising level in mV. as a function of the odour from a sample, where the odour is measured as an amount of H_2S in parts per million,

FIG. 5 is a schematic illustration of a test apparatus, and

FIGS. 6-20 are schematic illustrations of graphs representing test results.

DESCRIPTION OF EMBODIMENTS

FIG. 1 is an illustration of a method 102 and system in accordance with an embodiment of the invention. The figure illustrates the method 102 of controlling an amount of odour 104 from a liquid 106 having organic content, such as animal manure, slurry or waste water placed in a receptacle 128. In the example the liquid is animal manure. The method includes adding 110 an oxidising agent, such as air and/or ozone 108 with a system 130, to the liquid in order to reduce or eliminate its odour. The method further includes the methods step of monitoring a level 112 of oxidation of the liquid, and the method step of monitoring a slope 114 of change in the level of oxidation of the liquid and stopping adding 116 oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit in response to the slope and at least one criterion correlated to the slope of change of the level of oxidation.

In particular it has been found and it is illustrated that at a level of oxidation 113 of more than a predetermined level, such as minus 200 mV, said slope of change decreases from a relatively high first level 118 to a relatively low second level 120. Furthermore it has been found and it is shown that said slope of change upon adding further oxidising agent changes from the relatively high first level 118 to a relatively low second level 120 for a second time 124 at an oxidation level of the liquid of about minus 80 mV. It follows from the illustration that a first time 122 when the slope changes from a relative high level to a relatively low level is around -300 mV.

But in accordance with the invention it is the second time 124 which is important to monitor and notice the occurrence of, in order to eliminate the odour from the liquid in an efficient, stable and sturdy manner. This is due to that it has been found that upon occurrence of this second time the slope changes from a relative high level to a relatively low level, or when it does so at a level above minus 200 mV. then; the odour from the manure is eliminated. The amount of odour from the manure measured in parts per million of hydrogen sulphide, H_2S, from the manure is illustrated in figure 4.

Figure 1 also illustrates a control system 132. The control system includes a feed back mechanism. The control system includes an oxidation level sensor 134 adapted to sense a level of oxidation of the liquid in the receptacle and an oxidising agent sensor adapted to sense an amount and/or a rate of oxidising agent added to the liquid in the receptacle. The oxidation level sensor is illustrated as two wires in direct contact with the liquid and as such able to measure an oxidation or redox potential of the liquid.

Furthermore the control system includes a means, such as a valve 126, for controlling an amount and/or rate of oxidising agent to be added to the liquid in the receptacle. The means for controlling an amount and/or rate of oxidising agent to be added to the liquid may additionally or alternatively and as another example be a means for stopping generation of oxidising agent such as a means for shutting of an ozone generator.

The control system 132 is adapted to control an amount and/or rate of oxidising agent to be added to the liquid in the receptacle in order to control the amount of

odour from the liquid by being adapted to monitor a level of oxidation of the liquid in the receptacle 128 with said oxidation level sensor 134 and by being adapted to monitor the amount of oxidising agent added to the receptacle with said oxidising agent sensor and by being adapted to stop adding oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit with said means, such as a valve 126, in response to the slope of change in the oxidation level and at least one criterion correlated to the slope of change of the level of oxidation.

FIG. 2 is a graph showing an oxidation level in mV of six different samples of liquid as a function of an amount of oxidising agent added to the liquid in mg./l. Thus in the figure there are shown six curves 202, 204, 206, 208, 210, 212 corresponding to measurements on the six different samples 202, 204, 206, 208, 210, 212 upon addition of the oxidising agent ozone to each sample.

For the six different animal manure samples embodied as different types of liquids herein the level of oxidation when the odour is eliminated is approximately -25 mV, -40 mV, -50 mV, -75 mV, -80 mV and -100 mV, for the samples 202, 204, 206, 208, 210, 212, respectively. The samples are all animal manure samples, but factors and conditions such as the type of animal and dry matter concentration etc in the samples differs. When the measurements are provided with oxygen as oxidising agent, an amount of oxygen would be higher but e.g. a ratio between the relatively high slope and the relatively low slope is more or less the same as in the example with ozone. Similarly, when the liquid is not animal manure but e.g. effluent from households or an industrial factory, the oxidation levels as found with animal manure are not useable as criteria for when to stop addition of oxidising agent, whereas the ratio between relatively high slope and the relatively low slope is.

For the sample 208 the relatively high first level 118 of the slope or 'slope of change' is about 34 and the relatively low second level 120 of the slope is about 3.5. Thus, a ratio between the relatively high level of the slope and the relatively low slope of about 10 is found and thus, more than 25 divided by 10. For the six samples 202, 204, 206, 208, 210, 212, the amount of ozone added when the odour is eliminated is about 6 or 7 mg, 8 mg, 12 mg, 16 mg, 17 mg and 23 mg respectively. As previously discussed herein, and in that the oxidation level of certain liquids may decrease again rather rapidly, such as decrease 5 mV during a period of 24 hours, addition of oxidising agent may not be stopped or completely

stopped when this exact amount of oxidising agent has been added, but a minor amount of additional oxidising agent may additionally be added, possibly in order to give the liquid a certain odour free storage period. Alternatively, only a reduced amount of oxidising agent sufficient to maintain an odour free oxidation level is added per time unit.

Thus, it has been found and figure 2 and 3 in view of figure 4 illustrate, supports, demonstrates and discloses that either criteria a) or criteria b) can be used to provide an efficient control of the odour.

FIG. 3 is a graph 302 showing at least part of the curve showing the oxidation level 113 in mV of the sample 208 as a function of an amount of oxidising agent added to the liquid in mg/l 115. The graph is identical to the somewhat smaller illustration of the curve for the sample 208 which is part of figure 1. It is illustrated that at a moment when having added a given amount of ozone, i.e. in the present example about 16 mg ozone per litre animal manure, a tangent to the curve and pointed towards with the arrow 120 and thus a line correlated to the slope of the relatively low slope 120 of the curve for the sample 208 and another tangent to the curve shown and pointed towards with the arrow 118 and thus a line correlated to the relatively high slope 120 of the curve, intersects each other in a point 304. This point of intersection of tangents to the curve to a part of the curve with the relatively low slope and the relatively high slope, respectively, may alternatively be used as an alternative or further indicator of at which level of oxidation no more oxidising agent needs to be added in order to eliminate the odour from the liquid. In the present example the point has the coordinates of about (-75 mV , 16 mg/l).

FIG. 4 is a graph showing the oxidation level in mV 113 as a function of the odour from the sample 210. The odour is measured as and found to correspond to an amount of hydrogen sulphide emitted from the liquid in parts per million 404. It follows that at a level of oxidation of the liquid of less than -200 mV. 10 ppm H_2S can be measured and the liquid is found to smell or give an odour. At an oxidation level of -80 mV. the amount of emission of H_2S is measured to about 0.5% thereof and thus to about 0,05 ppm and the liquid is found not to smell or 'not to give odour'.

A number of experiments have been performed for determining that the observed changes in redox and H2S emission arises due to addition of an oxidant. This was confirmed by comparative studies where an inactive gas and mixing, which did not provide the results achieved by using a method according to the present invention. There was a clear connection between development of redox and H2S-emission when adding both O2 and O3. In the graphs it is seen that the redox curves have a rapid increase initially with a subsequent levelling. The corresponding curve for H2S has an initial short increase but a subsequent drop where after the curve flattens. The break is substantially coincident. This is an indication that the redox is a useful indication of the H2S emission.

A similar dependency was not observed when adding KMnO4.

Two types of test were performed, gas-tests and addition of KMnO4.

The gas-test was performed measuring the H2S concentration in headspace of the reactor using a hydrogen sulphide analyser, a Jerome 631 from Arizona Instruments LLC. The upper limit for the instrument used was 50 ppm. Higher values are reported as HL, i.e. High Levels. All measurements where HL is indicated are reported as 50 ppm. Gas-chromatography is performed using chemiluminescence detector (GC-SCD). The samples was initially stored in Tedlar-bags for 6 minutes before the test and after stored in the bags for detection of H2S using the GC-SCD. All samples where extracted during stirring.

Addition of KMnO4.
These tests were performed in a 5L jar covered with a plastic lid. The manure was stirred by Heidolph stirrer at 85 rpm. The test volume was 2 L and an airflow of 1 L/min at the surface was maintained in these tests. The H2S measurements were performed 10 cm above the surface of the manure but no samples for the GC-SCD were collected. This set-up was needed as it took approximately 30 minutes for the redox to stabilize when adding the additive in the reactor and redox quickly reduced after supplying the additive, especially in the range near 0 mV precise measurements were difficult. KMnO4 was added in batched of 0,1-1 mL from a freshly made 0,2M-solution.

Fresh manure from pigs in the experiments shed in Foulum were used. The samples contained some straw. The slurry was collected in two 60 L barrels and

the day after sampling divided into 10 bins each with 10 L slurry and frozen ~ -19 ^{0} C. Each treatment was performed three times. A bin of manure was taken out of the freezer the day before each experiment and thawed for the next morning. On the day of the experiments in the morning the slurry was divided into 3x2 L flasks, and samples of the thawed, untreated slurry were taken as a reference to the treated slurry. Additionally, 1 sample of 10 g dissolved in acetate (20%) for later analysis of sulfide. When the sample temperature typically was about 9-10 ° C from morning and most could rise to 15 ° C before the last repetition, all samples were tempered to 20-23 ° C in a water bath before beginning treatment.

Acidification: 7-8 L of the thawed slurry was acidified to approximately pH 5.5 with concentrated sulfuric acid (approximately 1.5 mL of acid per. L slurry). For O2 samples were acidification day before, while the other was performed on the day.

Addition of gas

2 L slurry was treated in a reactor with constant stirring and addition of gas through a diffuser at the bottom (see Figure 1). Before treatment was slurry with stirring for 15-20 min to achieve a stable redox value. Outlet for hydrogen sulfide measurement with Jerome and gas sampling and inlet for surface air-flow was located 10 cm above the manure surface. Redox and pH electrode was inserted into the reactor tube through a rubber seal and measured 7-8 cm below the slurry surface. Gas was injected with a flow of 0.06 L / min for all samples through the diffuser. The gas above the slurry (headspace) was replaced with an air flow 1L/min.

Fig. 5 is a schematic illustration of a test setup.

Fig. 6 is a schematic graph illustrating test results of the redox levels as a function of time. The test results was measured on a sample where a measure of N2 was added to raw-slurry and to acidified slurry, where the slurry was acidified by addition of H2SO4. The duration of the test was 80 minutes.

In the figure it may be seen that the redox level has a tendency to a slight increase at the beginning of the addition of oxidizing agent. This is probably due to the presence of air in the diffuser-unit entering the slurry at the moment N2 addition starts. The redox drop slowly, and at the end of the treatment redox level

falls to a level lower than the starting level. It is concluded that this required an oxidant to induce an increase in redox, and the combination of gas-enrichment and mixing alone does not give any effect in relation to redox. Acidification with the addition of N2 leads to redox level starts at a higher redox value, but otherwise similar process as for N2 alone.

Fig. 7 schematically illustrates the simultaneously development in redox level and H2S emission. The H2S level increases in the beginning coherently with the increase in redox level where after the levels stabilize.

The increase in the beginning is most likely due to the fact that the first addition of gas causes a transfers of a portion of the slurry H2S (i.e. increased matter-transfer) before a stabilization of the system is achieved. It is concluded that this required an oxidant to induce an increase in redox, and the combination of gas-enrichment and mixing alone does not give any effect in relation to removal of H2S emissions. Fig. 7 illustrates the development of redox in the slurry and H2S in the headspace as a function of added amount of N2. Non-acidified slurry is used.

Fig. 8 schematically summarizes H2S emissions for all samples spiked with N2. In this case higher for the non-acidified slurry. There is no clear trend from the non-acidified manure and there is no immediate change in H2S emissions during processing. For the acidified slurry, there seems to be an increase in emissions with decreasing redox. Fig. 8 schematically illustrates changes in H2S emissions measured with Jerome, as described above, as a function of redox. HL-values are set at 50 ppm. Each point represents a single measurement.

Fig. 9 schematically illustrates GC-SCD measurements which confirm that the H2S concentration is not different before and after treatment. Fig. 9 schematically illustrates H2S concentration as a function of added N2, measured by GC-SCD. Measuring points are averages of 3 replicates and error lines indicate standard deviation.

It is surprising that the acidifying slurry has a lower emission than the non-acidified slurry. With lower pH in the acidified slurry it would be expected to result in a higher emission, since a larger proportion of the total sulfide will be on H2S

form. One possible explanation could be that the H2S is degassed during acidification and immediately before the capture of gas has begun.

Addition of O2

Fig 10 schematically illustrates that redox level is clearly increases as a function of added O2. Redox of the acidified samples are shifted approximately 100 mV to a starting value around-210mV, but despite this difference in starting point the end-point of the redox level in all samples are around 50-55 mV. It is noted that the two distinct jumps in redox found in the original experiment are not present here, the curves all have a small bend or break, about -180 mV for the non-acidified sample and around - 70 mV for the acidified sample. Note that the redox level of the samples in this study begins 50-100 mV above what was measured in the comparable samples in the initial trials. Redox development by the addition of O2 in the untreated slurry and acidified (H2SO4) untreated slurry. Treatment time was 70 min.

Fig. 11 schematically illustrates the simultaneous development of redox and H2S as a function of O2. As observed in control sample there is a tendency for H2S to rise at first, but then concentration decreases sharply before the curve breaks and concentration approaches a stable, low, level. Break in the redox curve seems to correspond to the break in H2S curve.

Fig. 12 schematically illustrates H2S concentration as a function of added O2, measured by GC-SCD. Measuring points are averages of 3 replicates and error lines indicate standard deviation. The figure illustrates the same trend in the development of H2S concentration found during the other experiments. The values are slightly lower than those measured with Jerome. Samples are taken over a longer time (6 min vs. 20-45 s to Jerome), and is thus an average over all variations in this interval, which can cause discrepancies between the two measuring methods. Furthermore, Jerome does not separate H2S from other reduced sulfur compounds, which may also cause a higher signal.

Fig. 13 schematically illustrates H2S concentration, the concentration falls in the range between -100 and -50 mV for the non-acidified samples, whereas the reduction in the acidified samples are shifted to the interval between -50 mV and 0 mV. The figure illustrates evolution of H2S emissions as a function of redox

measured with Jerome. HL-values are set at 50 ppm. Each point represents a single measurement.

Addition of O3

Figure 14 compares the redox cycle of two raw slurry samples, where a combination of O2 and O3 is added to the samples, with similar tests where pure O2 is added. It is seen that the curves are roughly coincident. It is therefore uncertain whether the changes in redox found by ozone ring of the samples is due to the addition of ozone, or whether the redox changes as a result of the large amount of O2 added with O3.

The level of redox and H2S as a function of added volume O3 corresponds to the development seen for the oxygenated samples, except that the H2S concentration in the O3-treated samples started at a lower value.

Figure 14 schematically illustrates redox level development by the addition of O2 and O2 + O3 in untreated slurry. Processing time was 60-70 min. The amount of O2 in the ozone enriched samples (P32 and P33) is calculated by calculating a O2 content (~ 98%) in the air flow from the measured concentrations of O3 (~ 2% O3)

Fig. 15 schematically illustrates development of redox in the slurry and H2S in the headspace as a function of added amount of O3. Non-acidified slurry.

Fig. 16 schematically illustrates development of H2S emissions measured with Jerome as a function of redox. Each point represents a single measurement.

Fig. 16 schematically illustrates the development of H2S emissions from the ozone enriched samples similar to that for the oxygenated samples, except that the initial value is lower and the concentration range where H2S reduces are therefore shorter. The non-acidified samples fall in the range between -100 to -50 mV, while the acidified falls from -50 to 50 mV.

Fig. 17 schematically illustrates H2S concentration as a function of added O3, measured by GC-SCD. Measuring points are averages of 2 replicates and error lines indicate standard deviation.

Fig. 17 schematically illustrates that H2S concentration decreases on average within the first 6 minutes of treatment for non-acidified samples, this may be due to the fact that O3 reacts faster with H2S than O2, and therefore an average decrease is observed rather than increase as is the case for O2, there are large standard deviation of O2 measurements, and it cannot definitively be conclude that there is a difference between the two treatments within the first 6 min. The slope of the acidified samples treated with O3 is the same as found in the O2-treated. For both O3-treated samples did not detect H2S at GC-SCD in the full treated samples.

Addition of KMnO4

Fig. 18 schematically illustrates a redox curve shown that the addition of gas is not reflected by the addition of KMnO4. The relationship appears to be partially linear but fluctuating redox some time during. The figure illustrates redox development by adding KMnO4 in untreated slurry and acidified (H2SO4) untreated slurry.

Fig. 19 schematically illustrates the progress of a single sample. There is a correlation between increasing and decreasing redox H2S concentration, but the redox curve has no immediate characteristics which can be used to identify the optimal dose of KMnO4 for reducing H2S emission. The figure illustrates progress of redox in the slurry and H2S in the headspace as a function of added volume of KMnO4. The sample is a non-acidified slurry.

Fig. 20 schematically illustrates that the trend in the H2S measurements are similar to that found for the addition of O2, and the redox range where the concentration in the non-acidified sample drops the most is in the range -200 mV to -150 mV, while for the acidified is significantly broader and ranging from - 150 to 0mV. The figure illustrates the progress of H2S emissions measured with Jerome as a function of redox. HL-values are set at 50 ppm. Each point represents a single measurement.

Although the present invention has been described in connection with preferred embodiments, it is not intended to be limited to the specific form set forth herein. Rather, the scope of the present invention is limited only by the accompanying claims.

In short it is herein disclosed that in order, e.g., to provide a method of and system for treating various types of liquid having organic content, such as various types of animal manure, in a manner which provides a stable and sturdy result, also when certain conditions changes or varies, there is provided a method 102 of controlling an amount of odour 104 from a liquid 106 having organic content comprising adding 110 an oxidising agent, such as air and/or ozone, to the liquid in order to reduce or eliminate its odour, and monitoring a level 112 of oxidation of the liquid, and monitoring a slope 114 of change in the level of oxidation of the liquid, and stopping adding 116 oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit in response to the slope of change of the level of oxidation and at least one criterion correlated to the slope.

In this section, certain specific details of the disclosed embodiment are set forth for purposes of explanation rather than limitation, so as to provide a clear and thorough understanding of the present invention. However, it should be understood readily by those skilled in this art, that the present invention may be practised in other embodiments which do not conform exactly to the details set forth herein, without departing significantly from the spirit and scope of this disclosure. Further, in this context, and for the purposes of brevity and clarity, detailed descriptions of well-known apparatus, circuits and methodology have been omitted so as to avoid unnecessary detail and possible confusion.

In the claims, the term "comprising" does not exclude the presence of other elements or steps. Additionally, although individual features may be included in different claims, these may possibly be advantageously combined, and the inclusion in different claims does not imply that a combination of features is not feasible and/or advantageous. In addition, singular references do not exclude a plurality. Thus, references to "a", "an", "first", "second" etc. do not preclude a plurality. Reference signs are included in the claims, however the inclusion of the

reference signs is only for clarity reasons and should not be construed as limiting the scope of the claims.

CLAIMS

1. A method (102) of controlling an amount of odour (104) from a liquid (106) having organic content, such as animal manure, slurry or waste water, the odour originates at least partly from hydrogen sulphide in the liquid, where the method comprises adding (110) an oxidising agent, such as air and/or ozone, to the liquid in order to reduce or eliminate its odour, and wherein the method further comprises

- monitoring a level (112) of oxidation of the liquid, and
- monitoring a slope (114) of change in the level of oxidation or redox potential of the liquid over time, and
- stopping adding (116) oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit in response to the slope of change of the level of oxidation or redox potential and at least one criterion correlated to said slope.

2. The method according to claim 1, wherein the at least one criterion for stopping adding (116) oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit is achieved when or just after

a) at a level of oxidation (113) of more than a predetermined level, such as minus 200 mV., said slope of change decreases from a relatively high first level (118) to a relatively low second level (120) or when or just after
b) at any level of oxidation, said slope of change changes from the relatively high first level (118) to a relatively low second level (120) for a second time (124).

3. The method according to any of the preceding claims, wherein the level of oxidation (113), when stopping adding oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit, is in an interval from and including minus 150 mV to and including minus 25 mV, such as about minus 80 mV.

4. The method according to any of the preceding claims 2 or 3, wherein the oxidising agent is ozone and where the relatively high first level (118) of the slope is more than and including 25 mV pr. mg ozone added per volume unit of the liquid and wherein the relatively low second level (120) of the slope is less than and including 10 mV pr. mg ozone added per volume unit of the liquid (106).

5. The method according to any of the preceding claims, wherein stopping or reducing addition of oxidising agent is provided when a ratio between said relatively high first level and said relatively low second level is equal to or more than 25 divided by 10.

6. The method according to any of the preceding claims, wherein the oxidising agent is ozone and where initially only about 0.5 to 4 mg ozone is added per litre of the liquid (106).

7. The method according to claim 6, wherein an amount of ozone added per volume unit of the liquid is increased from the initial added amount of ozone in increments below 3 mg ozone per litre of the liquid (106).

8. The method according to any of the preceding claims, wherein the oxidising agent is ozone and where the amount of ozone added per volume unit of the liquid (115) and per treatment is in the interval from and including 0.5 mg ozone per litre of the liquid to and including 27 mg ozone per litre of the liquid.

9. The method according to any of the preceding claims, wherein the odour (104) from the liquid is considered to be reduced or eliminated when an emission (404) measured in a number of parts per million of hydrogen sulphide from the liquid is below 0.1 parts per million.

10. The method according to any of the preceding claims 1-5, 8 or 9, wherein there is continually added an amount of oxidising agent to the liquid (106) per time unit and per volume unit of the liquid until the addition of oxidising agent is stopped or reduced.

11. The method according to any of the preceding claims, wherein the method further comprises starting adding oxidising agent to the liquid or increasing addition of oxidising agent to the liquid per time unit in response to the oxidation level.

12. An apparatus for controlling an amount of odour (104) from a liquid (106) having organic content, such as animal manure, slurry or waste water, where the apparatus comprises

- a receptacle (128) for the liquid (106),

- a system (130) for adding an oxidising agent, such as air and/or ozone, to the liquid
- a control system (132) with a feed back mechanism, and wherein the control system comprises
  - an oxidation level sensor (134) adapted to sense a level of oxidation of the liquid in the receptacle
  - an oxidising agent sensor adapted to sense an amount and/or a rate of oxidising agent added to the liquid in the receptacle
  - a means, such as a valve (126), for controlling an amount and/or rate of oxidising agent to be added to the liquid in the receptacle and wherein

the control system (132) is adapted to control an amount and/or rate of oxidising agent to be added to the liquid in the receptacle in order to control the amount of odour from the liquid by being adapted to monitor a level of oxidation of the liquid in the receptacle (128) with said oxidation level sensor (134) and by being adapted to monitor the amount of oxidising agent added to the receptacle with said oxidising agent sensor and by being adapted to stop adding oxidising agent to the liquid or reducing an amount of oxidising agent added per time unit with said means, such as a valve (126), in response to a slope of change of the level of oxidation and at least one criterion correlated to said slope.

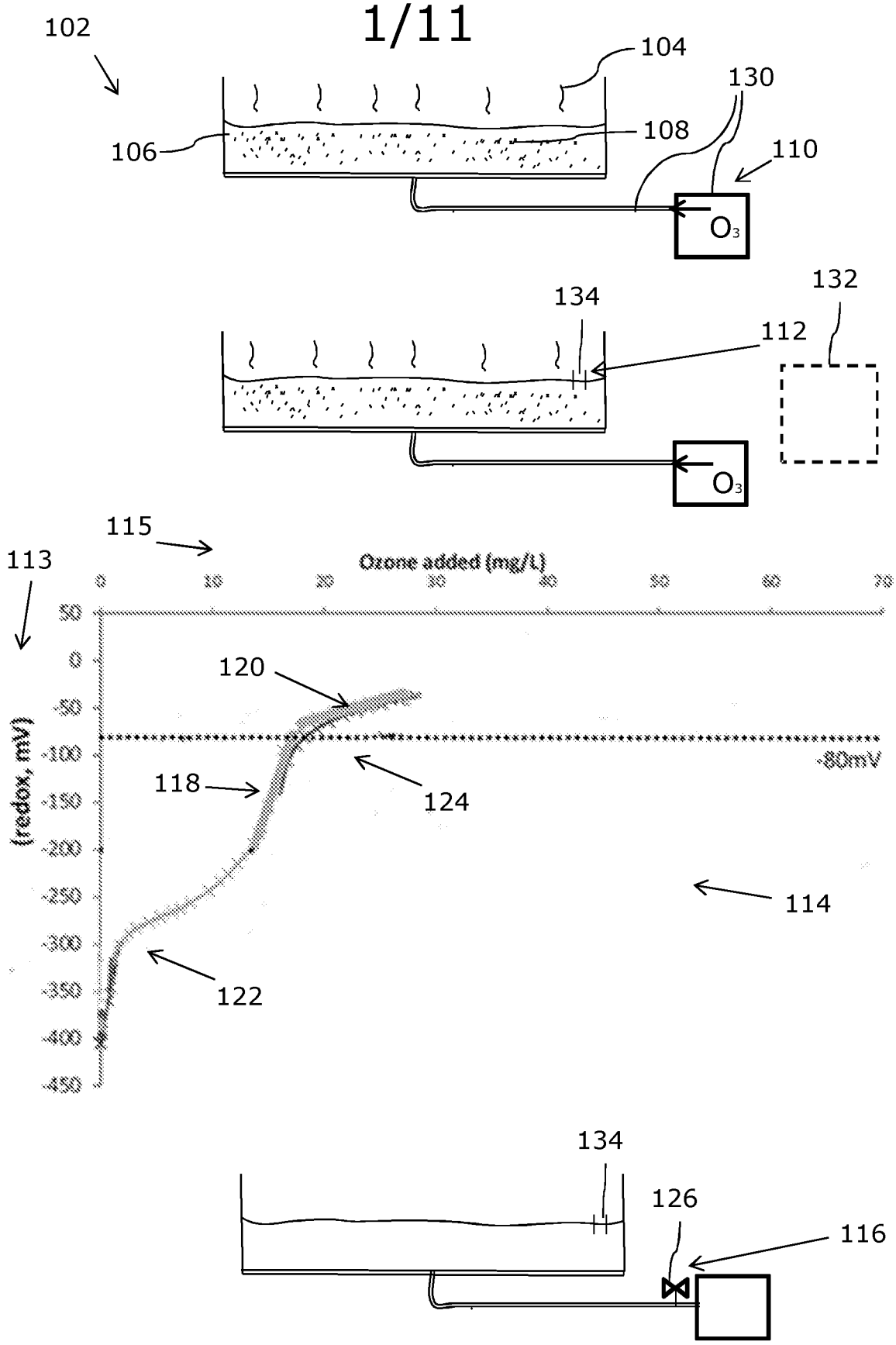

102
104
130
106
108
110
O_3
132
134
112
O_3
115
113
Ozone added (mg/L)
0
10
20
30
40
50
60
70
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
(redox, mV)
120
-80mV
118
124
114
122
134
126
116

FIG.1

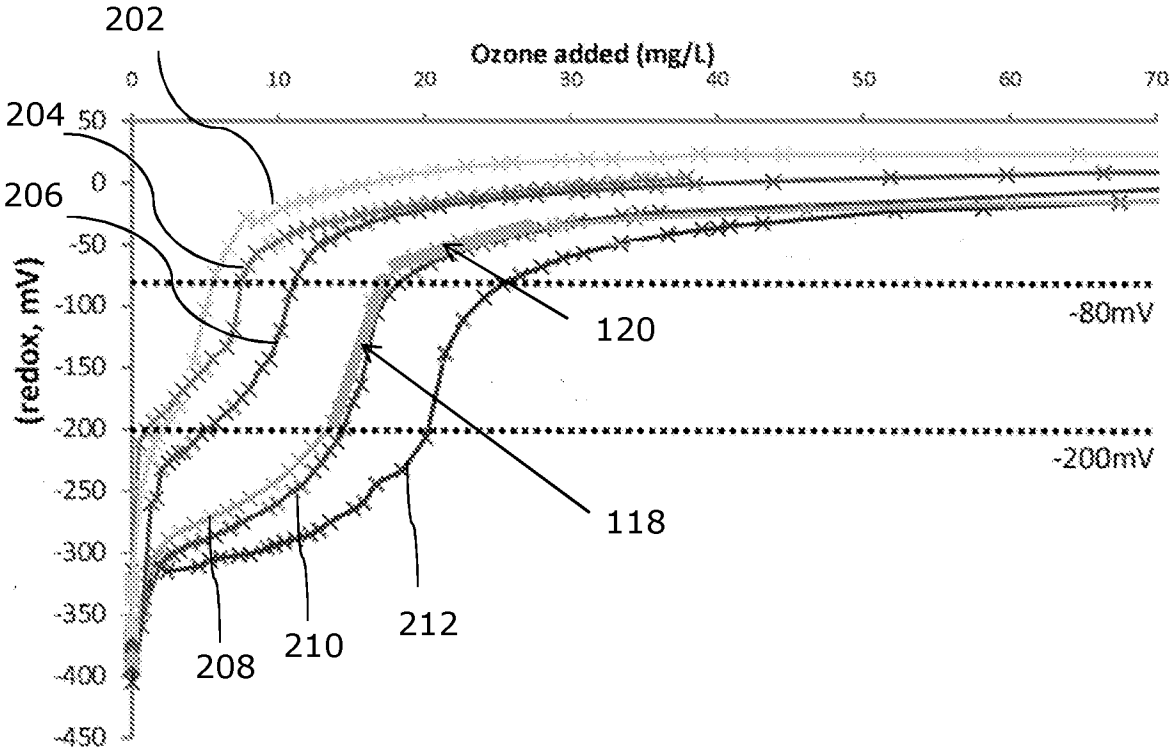

202
Ozone added (mg/L)
0
10
20
30
40
50
60
70
204
206
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
(redox, mV)
-80mV
-200mV
120
118
208
210
212

FIG.2

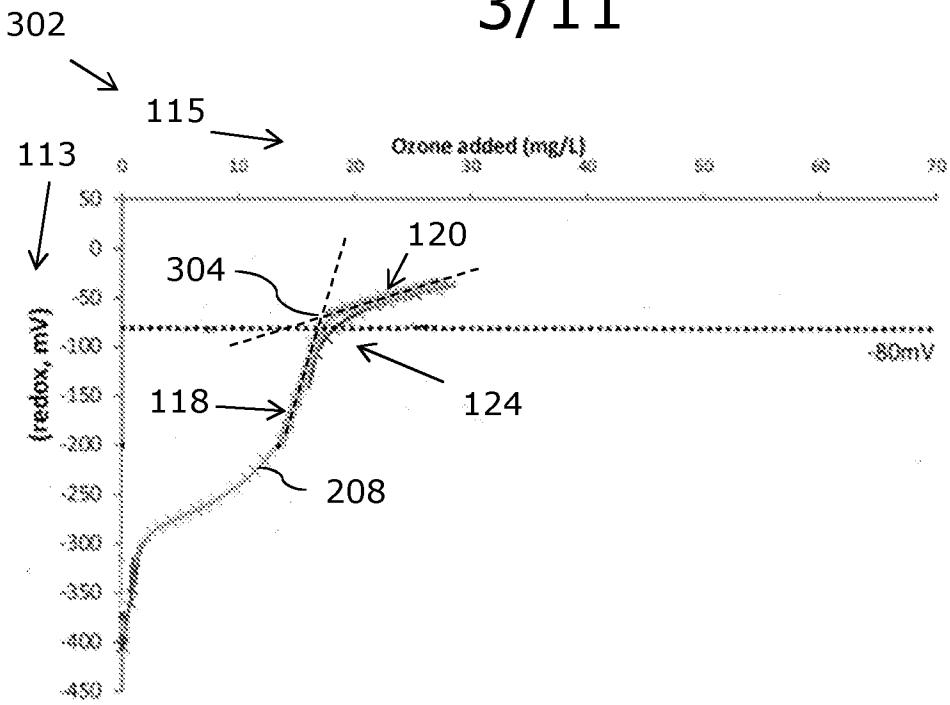

302
115
113
Ozone added (mg/L)
120
304
-80mV
118
124
208
(redox, mV)

FIG.3

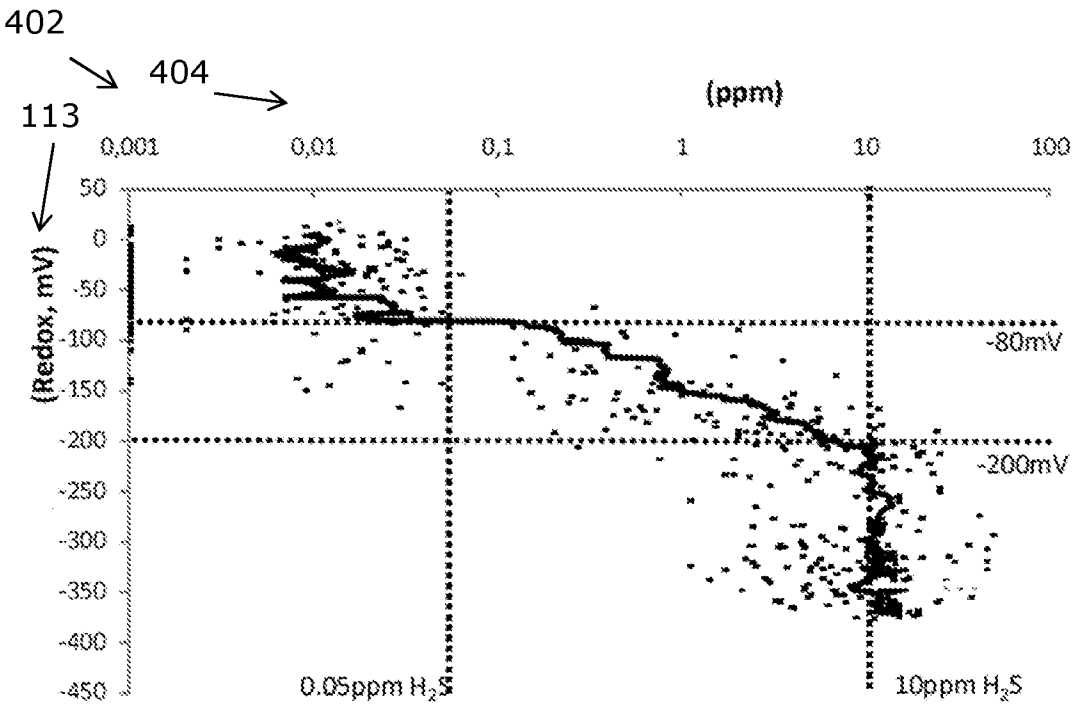

402
404
113
(ppm)
0,001
0,01
0,1
1
10
100
(Redox, mV)
-80mV
-200mV
0.05ppm H_2S
10ppm H_2S

FIG.4

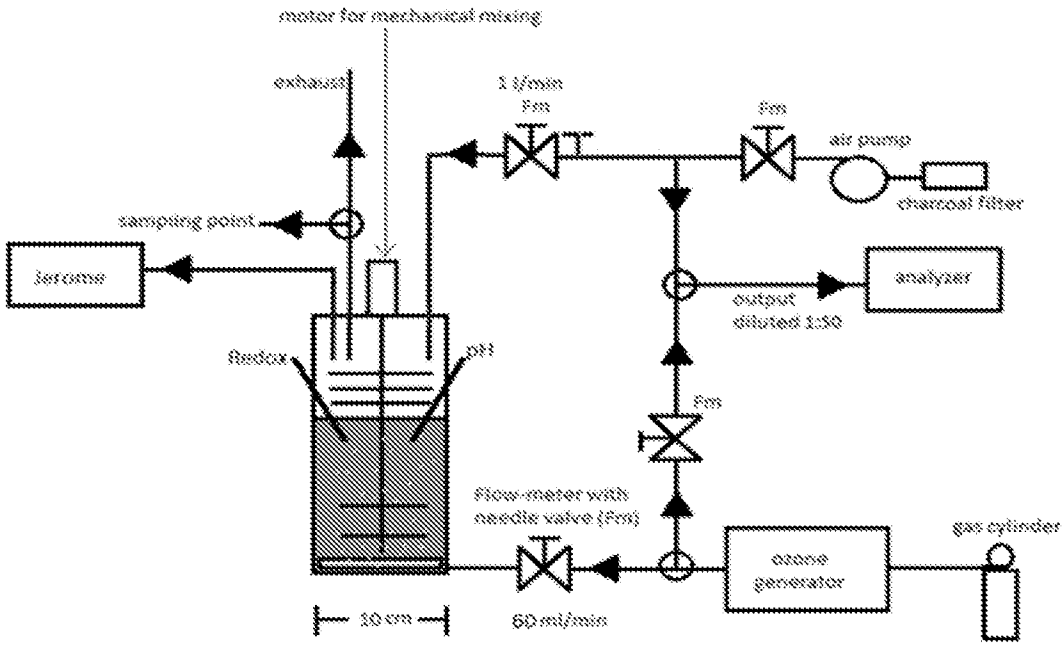

motor for mechanical mixing
exhaust
1 l/min
Fm
Fm
air pump
charcoal filter
sampling point
Jerome
analyzer
output
diluted 1:50
Redox
pH
Fm
Flow-meter with
needle valve (Fm)
ozone
generator
gas cylinder
10 cm
60 ml/min

FIG.5

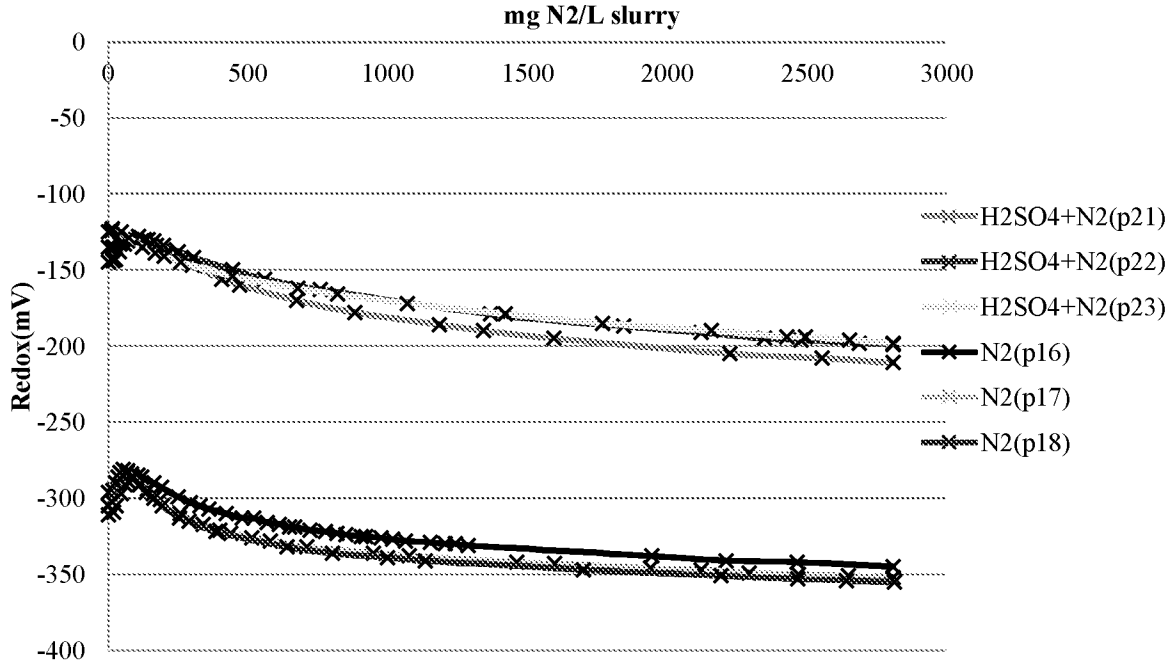

mg N2/L slurry
0
500
1000
1500
2000
2500
3000
-50
-100
-150
-200
-250
-300
-350
-400
Redox(mV)
H2SO4+N2(p21)
H2SO4+N2(p22)
H2SO4+N2(p23)
N2(p16)
N2(p17)
N2(p18)

FIG.6

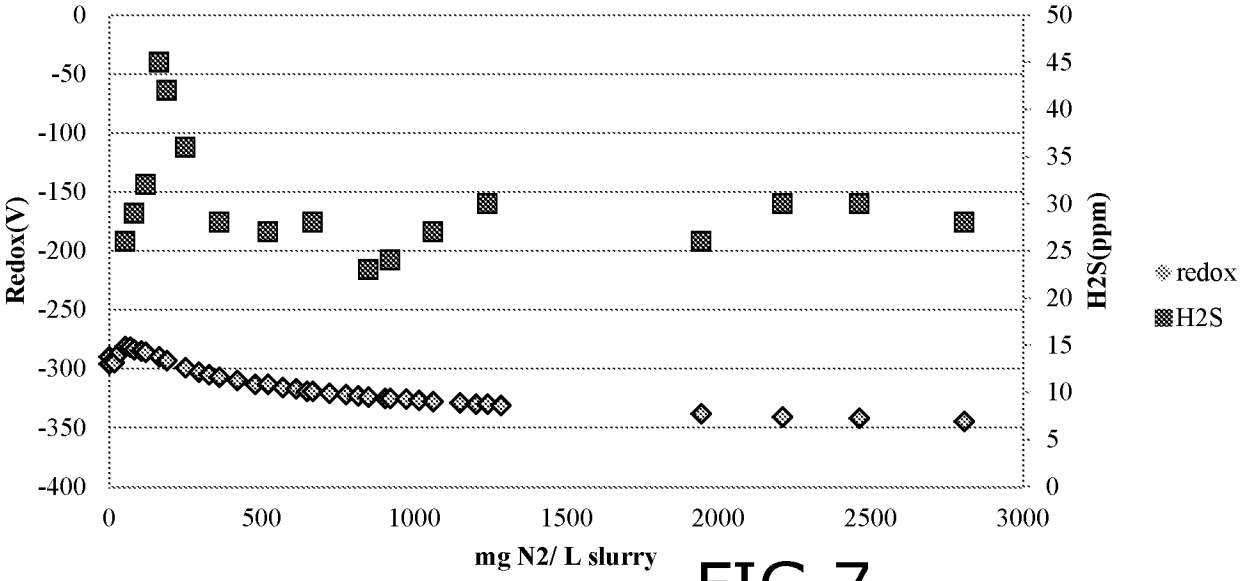

Redox(V)
H2S(ppm)
mg N2/ L slurry
redox
H2S
0
-50
-100
-150
-200
-250
-300
-350
-400
50
45
40
35
30
25
20
15
10
5
0
0
500
1000
1500
2000
2500
3000

FIG.7

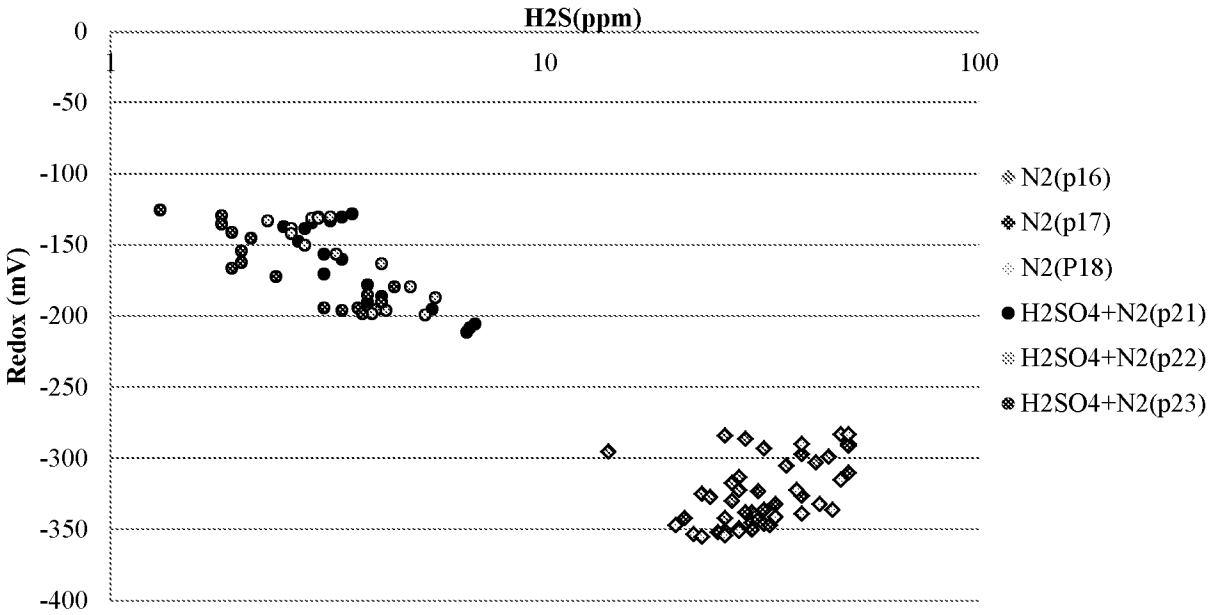

H2S(ppm)
Redox (mV)
0
1
10
100
-50
-100
-150
-200
-250
-300
-350
-400
N2(p16)
N2(p17)
N2(P18)
H2SO4+N2(p21)
H2SO4+N2(p22)
H2SO4+N2(p23)

FIG.8

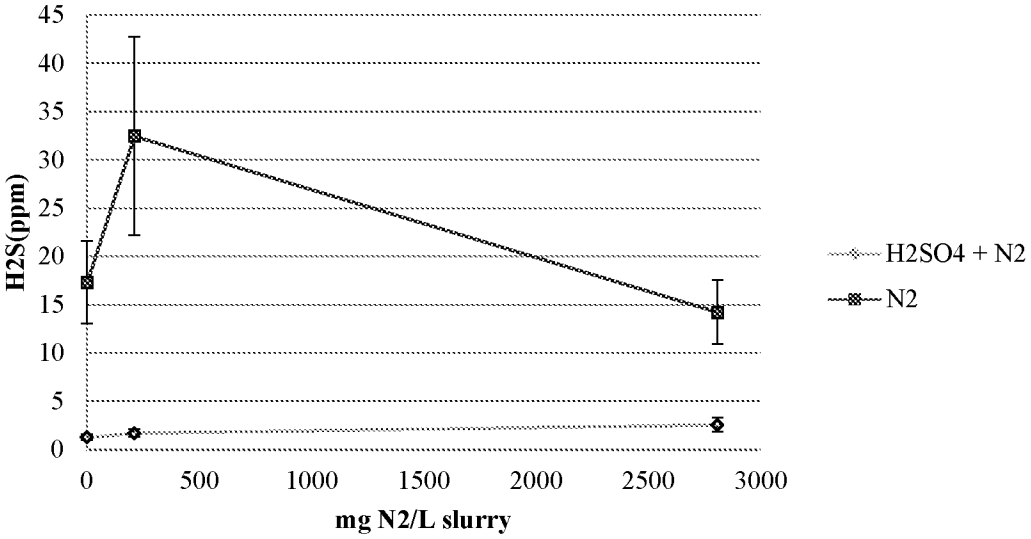

45
40
35
30
25
20
15
10
5
0
H2S(ppm)
0
500
1000
1500
2000
2500
3000
mg N2/L slurry
H2SO4 + N2
N2

FIG.9

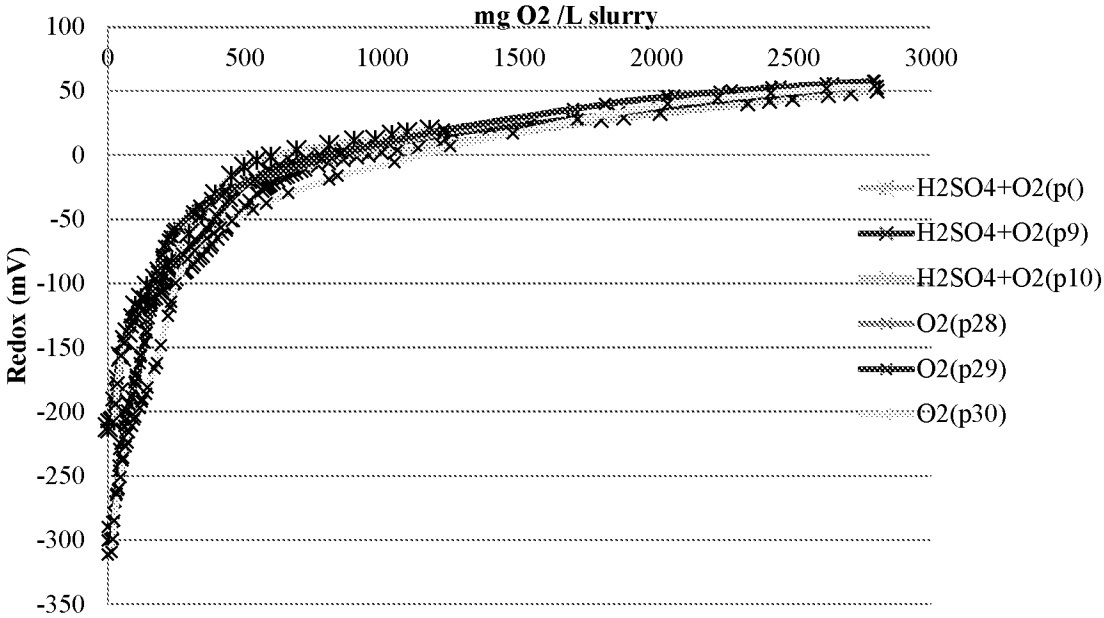

mg O2 /L slurry
100
50
0
-50
-100
-150
-200
-250
-300
-350
Redox (mV)
0
500
1000
1500
2000
2500
3000
H2SO4+O2(p()
H2SO4+O2(p9)
H2SO4+O2(p10)
O2(p28)
O2(p29)
O2(p30)

FIG.10

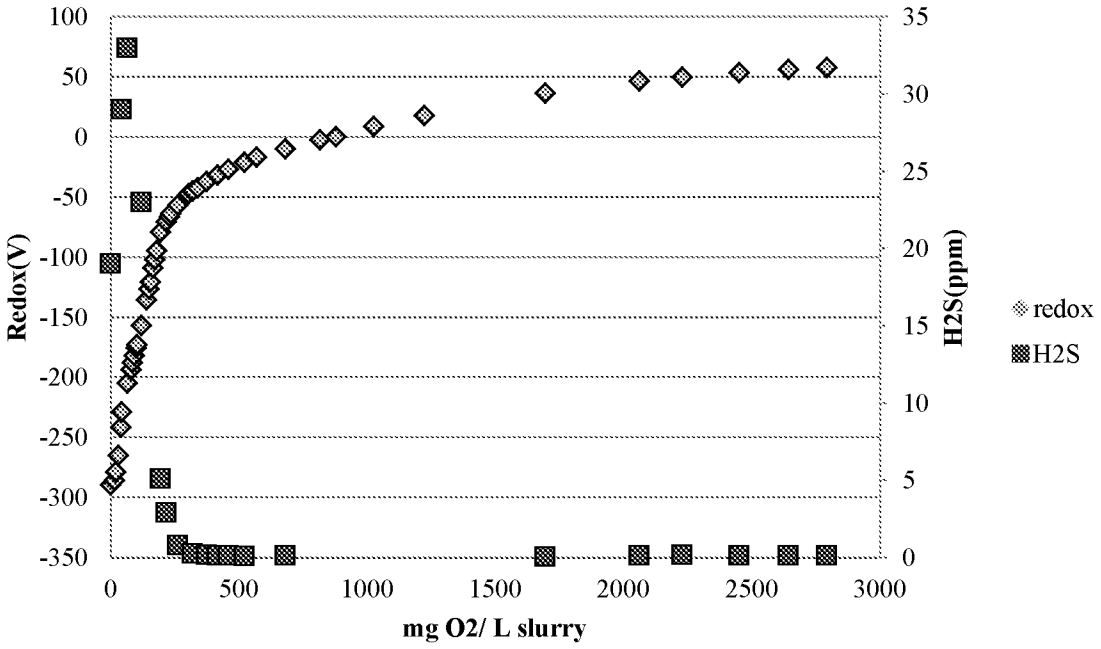

Redox(V)
H2S(ppm)
mg O2/ L slurry
redox
H2S

FIG.11

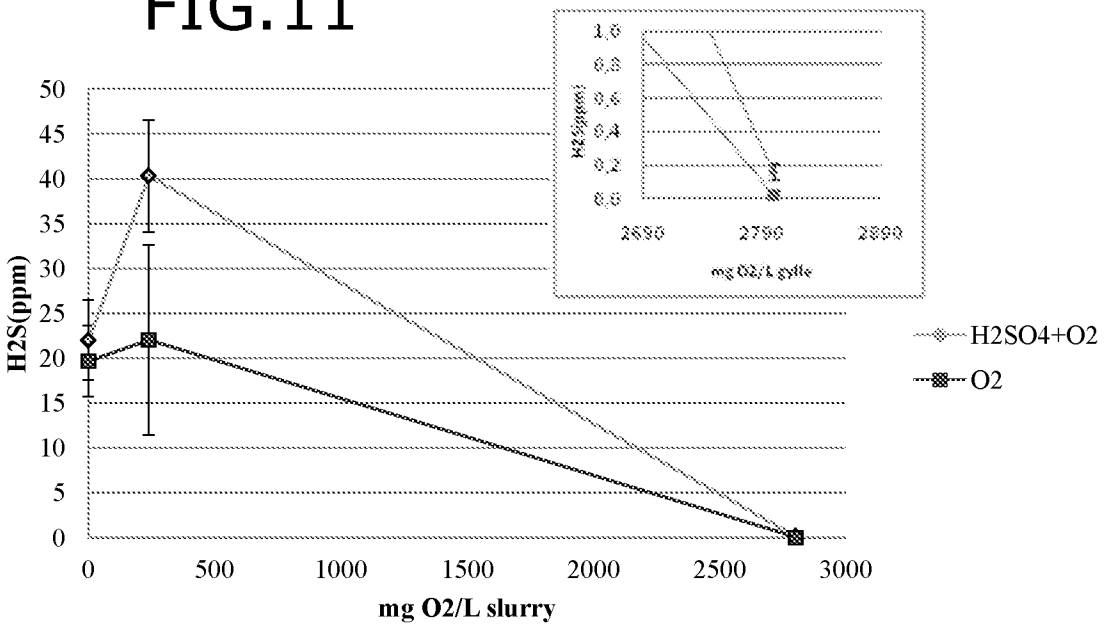

H2S(ppm)
mg O2/L slurry
H2SO4+O2
O2

FIG.12

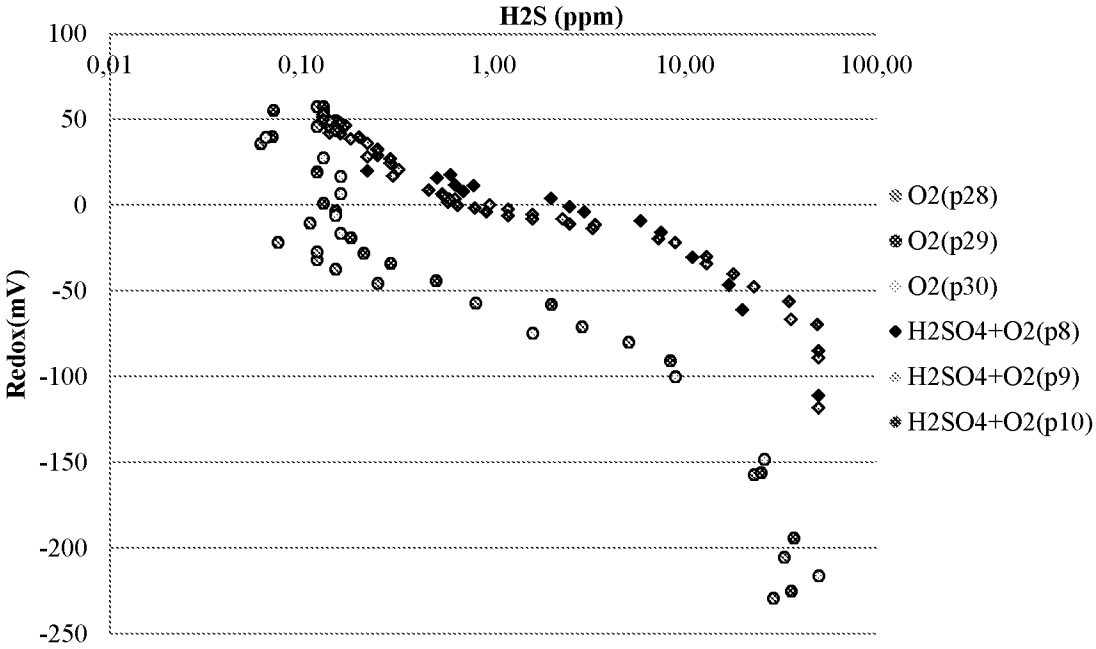

H2S (ppm)
100
0,01
0,10
1,00
10,00
100,00
50
0
-50
-100
-150
-200
-250
Redox(mV)
O2(p28)
O2(p29)
O2(p30)
H2SO4+O2(p8)
H2SO4+O2(p9)
H2SO4+O2(p10)

FIG.13

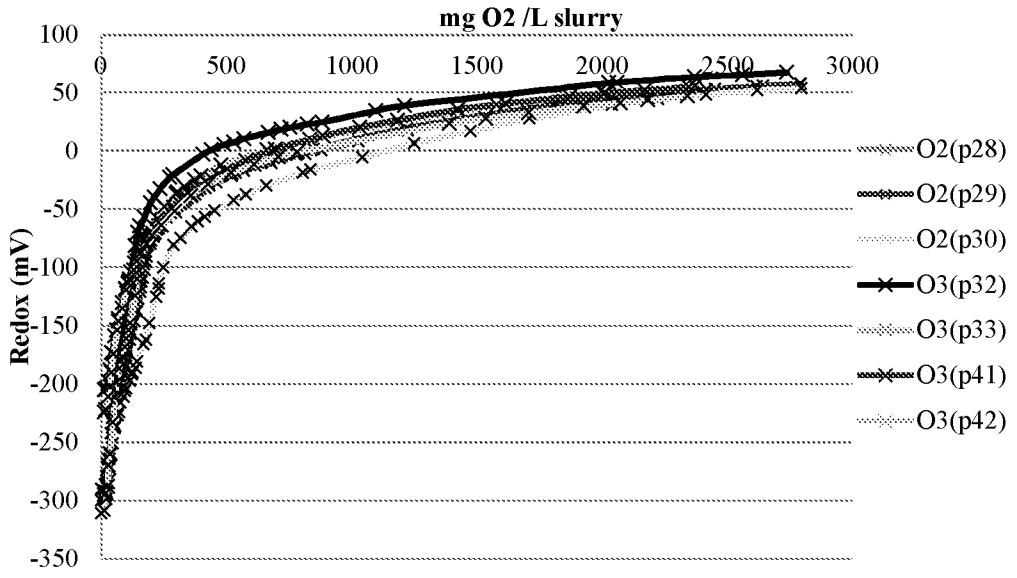

mg O2 /L slurry
100
0
500
1000
1500
2000
2500
3000
50
0
-50
-100
-150
-200
-250
-300
-350
Redox (mV)
O2(p28)
O2(p29)
O2(p30)
O3(p32)
O3(p33)
O3(p41)
O3(p42)

FIG.14

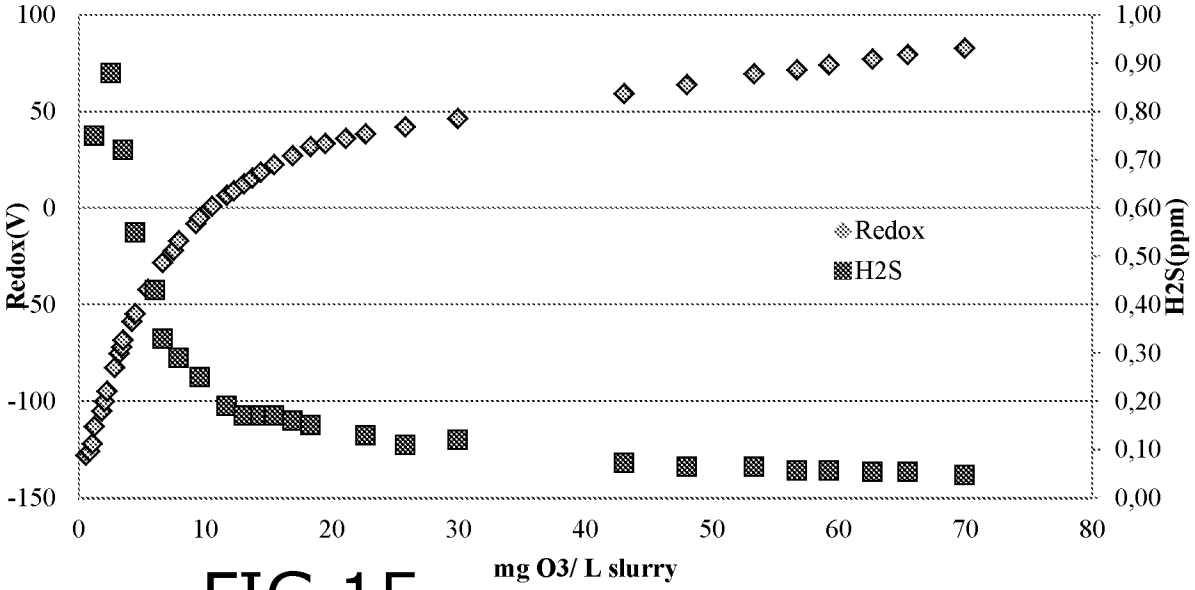

100
50
0
-50
-100
-150
Redox(V)
1,00
0,90
0,80
0,70
0,60
0,50
0,40
0,30
0,20
0,10
0,00
H2S(ppm)
Redox
H2S
0
10
20
30
40
50
60
70
80
mg O3/ L slurry

FIG.15

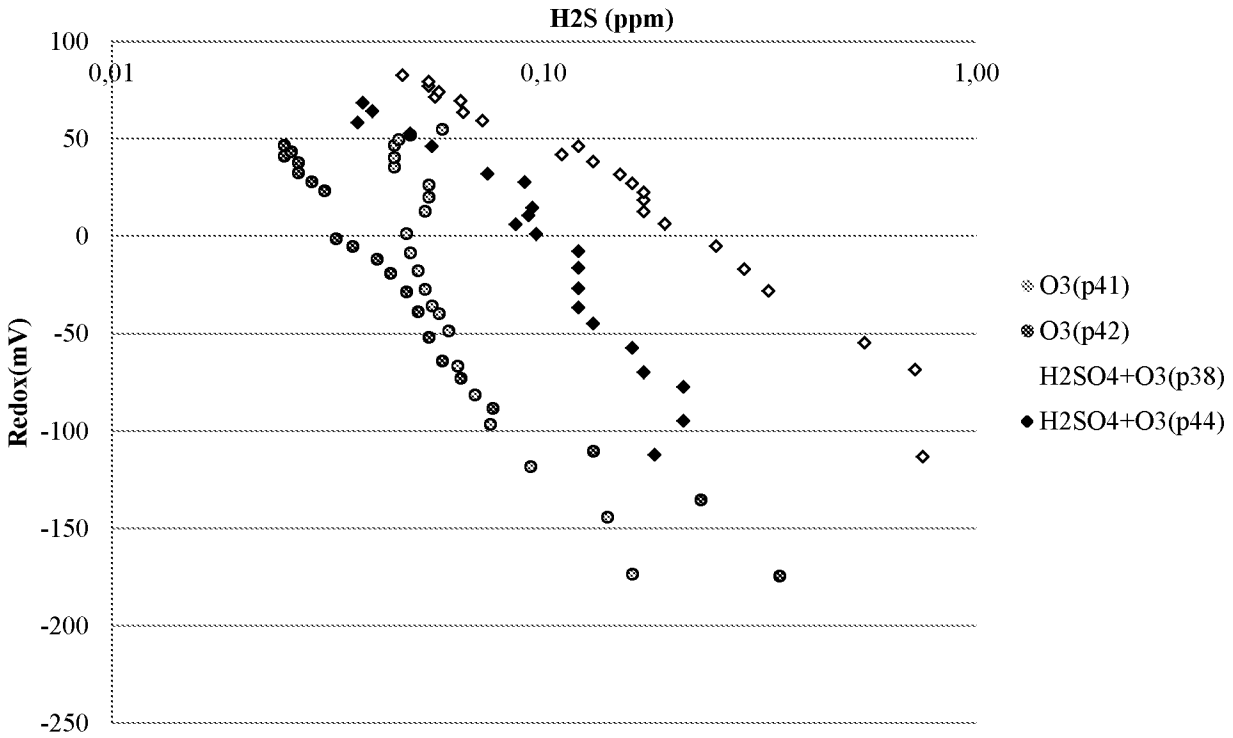

H2S (ppm)
100
0,01
0,10
1,00
50
0
-50
-100
-150
-200
-250
Redox(mV)
O3(p41)
O3(p42)
H2SO4+O3(p38)
H2SO4+O3(p44)

FIG.16

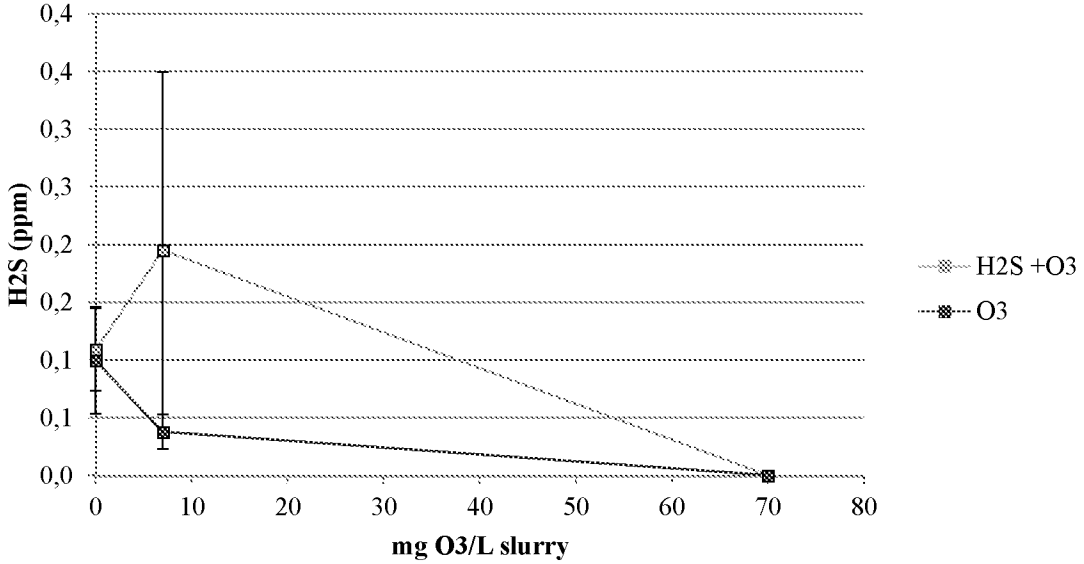

0,4
0,4
0,3
0,3
0,2
0,2
0,1
0,1
0,0
H2S (ppm)
0
10
20
30
40
50
60
70
80
mg O3/L slurry
H2S +O3
O3

FIG.17

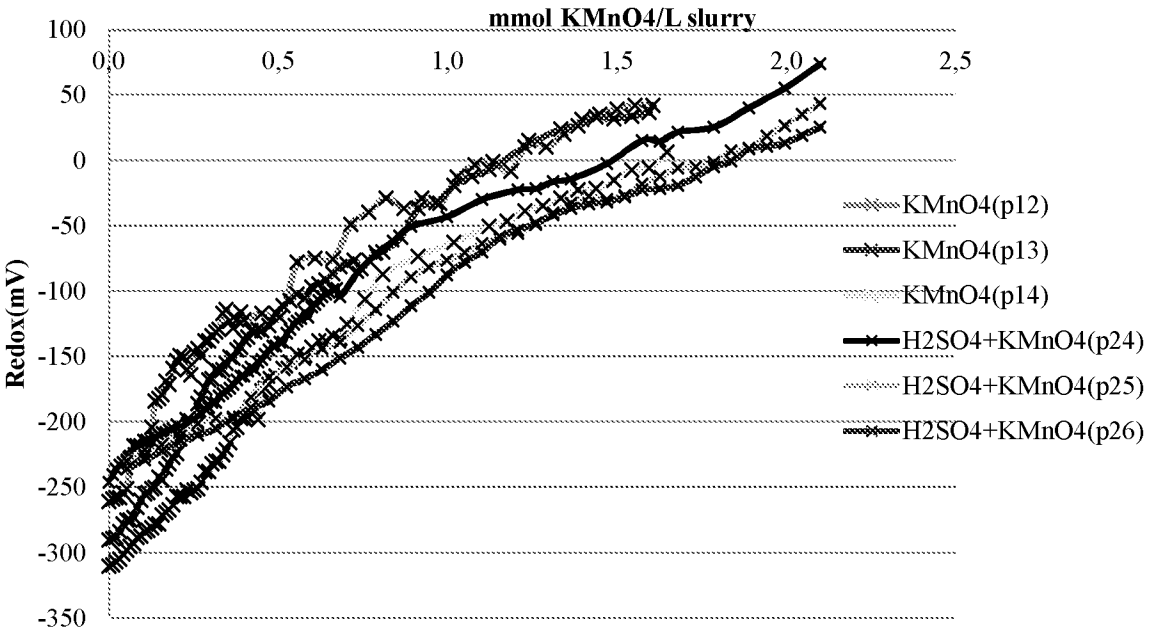

mmol KMnO4/L slurry
100
50
0
-50
-100
-150
-200
-250
-300
-350
Redox(mV)
0,0
0,5
1,0
1,5
2,0
2,5
KMnO4(p12)
KMnO4(p13)
KMnO4(p14)
H2SO4+KMnO4(p24)
H2SO4+KMnO4(p25)
H2SO4+KMnO4(p26)

FIG.18

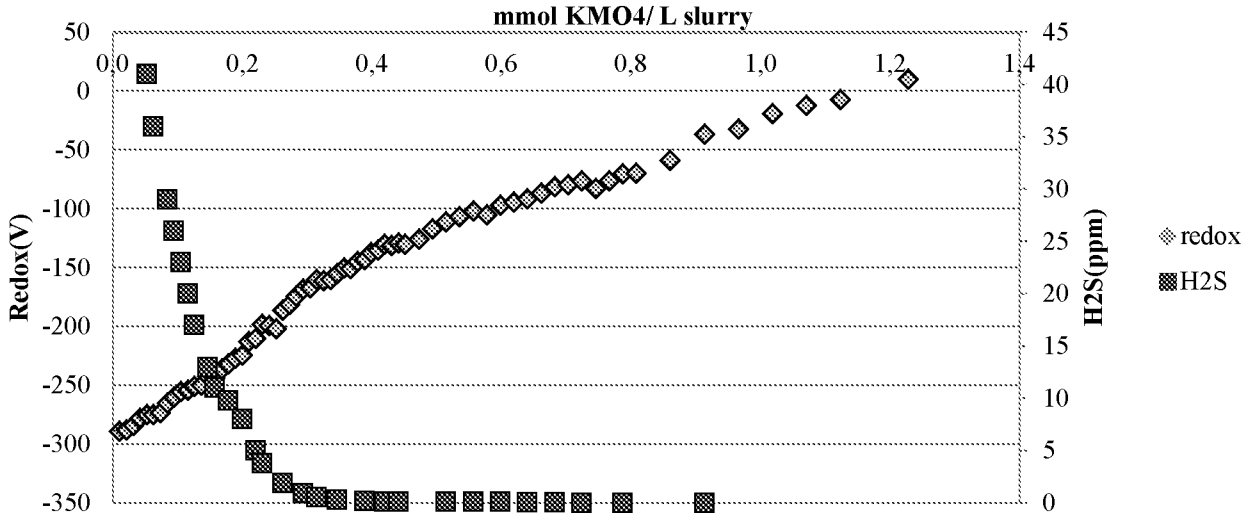

mmol KMO4/ L slurry
Redox(V)
H2S(ppm)
redox
H2S

FIG.19

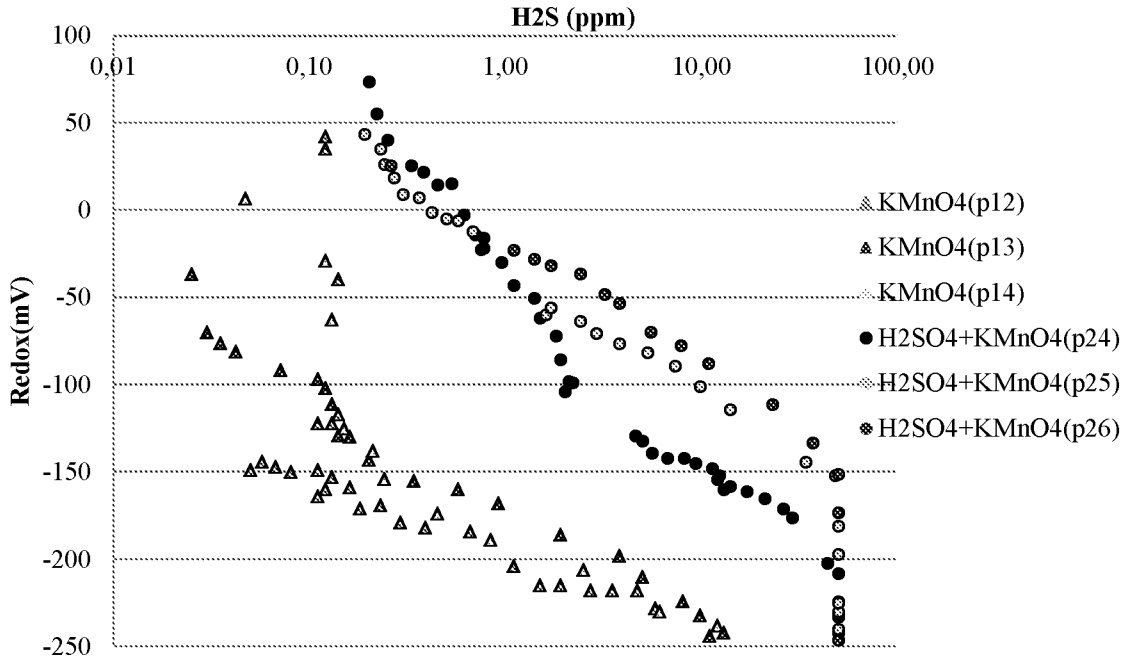

H2S (ppm)
Redox(mV)
KMnO4(p12)
KMnO4(p13)
KMnO4(p14)
H2SO4+KMnO4(p24)
H2SO4+KMnO4(p25)
H2SO4+KMnO4(p26)

FIG.20

INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2011/050378

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/78
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 970 353 A1 (GUSTAFSSON RAGNVALD [SE] STROEMHAGE RAGNVALD [SE]) 17 September 2008 (2008-09-17) claims 1-16 paragraphs [0002] - [0003], [0005] - [0006], [0009] - [0010], [0014] figure 1 -----	1-12
X	DE 10 2007 054115 A1 (ECH ELEKTROCHEMIE HALLE GMBH [DE]) 20 May 2009 (2009-05-20) claims 1-17 paragraphs [0001] - [0002], [0009] - [0012] figures 1-4 ----- -/--	1-12

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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15 November 2011	23/11/2011

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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Galiana López, Paula

INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2011/050378

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/DK2011/050378

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