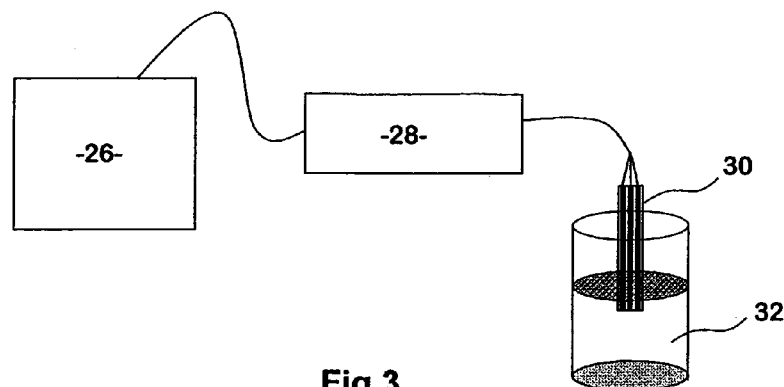


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[Continued on next page]

(54) **Title:** PREPARATION OF SETTING SLURRIES**Fig 3**

(57) **Abstract:** When preparing a settlable slurry such as a cement slurry for cementing an oil well, cement or other solid powder is mixed with water and a set retarder. In order to be able to run a convenient and rapid check on the concentration of retarder after dilution at the site of use, a tracer material is mixed with the retarder in known amount during manufacture. The tracer is chosen to enable its concentration to be determined analytically after dilution at the site of use, thereby providing a way to determine the concentration of set retarder after such dilution. The tracer may be a redox-active material and its concentration may be determined by voltammetry. Tracer may likewise be mixed with additives other than set retarder.



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Preparation of setting slurries

Field of the Invention

[0001] This invention relates to the preparation of slurries which set to solid form after they have been prepared. These may in particular, but not exclusively, be cement slurries used in wellbore cementing.

Background of the invention

[0002] Cement slurry is typically made by mixing cement powder, water (sometimes referred to as the mix-water) and various additives that may include retarders, dispersants, fluid-loss additives and anti-foam additives.

[0003] When the cement slurry is going to be used to fill the space between a drilled bore hole and a casing inserted into that borehole, the slurry must flow for a considerable distance before it reaches its final position where it is required to set. It is therefore normal to include a retarder to delay setting. Typically the retarder and other additives are supplied to the rig-site as manufactured products, which may be stock solutions, and these are added to the mix-water before adding the cement powder. So, when making up the mix water a stock solution of retarder might be diluted 100-fold or more.

[0004] It is very important that the correct amount of retarder is added. Using too much retarder will delay set of the cement unnecessarily and hence increase the “waiting on cement” delay during which the well site stands idle because further work cannot be done until the cement has set. On the other hand premature setting of the cement can be hugely expensive to rectify.

[0005] Yet, there is currently no satisfactory technology for checking that the concentration of retarder as diluted in the mix-water used to make the cement slurry is correct. The only available test is to take a sample of the mix water (with the additives in it, but before the cement powder is added) and run a thickening test either in a fixed laboratory which is not at the rig site or in a portable laboratory if available at the site of intended use. This process is time-consuming, potentially taking up to 8 or 9 hours (depending on the

thickening time) and so results in job delays and (depending on the outside temperature) in the possible degradation of the quality of the mix water.

Summary of the invention

[0006] The invention provides a way to check the concentration of an additive in a cement slurry and/or in the mix-water before cement powder is added. The invention can be embodied as a facile, inexpensive, and accurate measurement technique which can be carried out rapidly at the site of use without requiring a fully equipped laboratory. Although the invention has been conceived in the specific context of checking retarder concentration when cementing a wellbore, it could also be applied to other additives and /or in other contexts.

[0007] According to a first aspect of this invention a process of preparing a settable slurry comprises mixing a solid powder, water and one or more additives, and the process is characterised by

- mixing a tracer material with an additive before mixing that additive with the solid powder and the water and by
- analysing a mixture containing at least the additive and some or all of the water to determine the concentration of tracer therein.

[0008] The solid powder is likely to be a cement powder although it might possibly be some other material such as gypsum plaster which forms a settable slurry with water. The additive may be a set retarder for cement. An advantage of using a tracer substance which is not itself acting as retarder or functional additive is that there is then freedom to select the tracer as a substance which can be detected analytically.

[0009] It is envisaged that the tracer could be added to retarder or other additive at the manufacturer's factory, or could be added by a commercial intermediary or even by the end user while the additive is in storage prior to use. Addition of tracer while the additive is stockpiled as a concentrate could be checked by laboratory analysis if so desired.

[0010] When mixing cement at the site of the well to be cemented, the concentration of the tracer could be determined after mixing the retarder or other additive with the mix-water,

e.g. after mixing all the retarder with the calculated total quantity of water but before mixing with the solid cement powder. Alternatively or additionally the concentration of tracer could be determined in a sample taken from the mixed cement slurry which is ready to be placed in the position where it will set. It is also possible that the retarder or other additive might be mixed with some of the total quantity of water, but not all of it, and the concentration of tracer determined at that stage. Depending on the result, a further quantity of water might then be added to adjust the dilution.

[0011] It is possible that the tracer could be detected by a spectroscopic method, for example using a tracer with a distinctive fluorescence. For instance fluorescein has been used as a tracer in applications where the objective is to identify a path of flow. It exhibits strong fluorescence under visible or ultraviolet illumination and is thereby detectable at concentrations of 10ppm and even less, as for instance mentioned in Society of Petroleum Engineers paper 50768. A number of other fluorescent materials have been employed as tracers, including compounds of the lanthanide series of elements, as mentioned in US 5979245 and WO2007/102023.

[0012] In some preferred forms of this invention the concentration of tracer is determined by an electrochemical measurement. The tracer may then be a compound which is capable of undergoing electrochemical reduction and oxidation and the analytical procedure may use the current flow during this electrochemical oxidation and reduction to determine the concentration of tracer.

[0013] More specifically, the tracer may be determined by one of the available forms of voltammetry which applies potential to the electrodes and measures the current flow.

[0014] One possible form of voltammetry varies the potential applied to a working electrode over a sufficient range to bring about the oxidation or reduction reaction of the tracer while recording the current flow as the potential is varied. This form of voltammetry may be a linear scan over a range of applied potential or may be a cyclic scan over a range of potential and back again, so as to bring about both the oxidation and reduction of the tracer. A discussion of cyclic voltammetry can for instance be found in "Electrochemistry, Principles, methods and applications" by C M A Brett and A M O Brett (OUP 1993) pages 174-199. The recorded current shows peaks at the potentials associated with the

electrochemical reduction and oxidation. The concentration of the compound undergoing redox reaction, which for the present invention will be the compound acting as tracer, may be calculated from the observed current, may be found using a previously constructed calibration curve or look-up table, or may be determined by means of additional experiments with deliberately added tracer as illustrated in one of the Examples below.

[0015] Another possible form of voltammetry which may be used is square wave voltammetry in which the potential applied to a working electrode is provided by a square wave superimposed on a staircase baseline, so that the potentials applied at the peaks and troughs of the square wave increase progressively. Current flow is measured close to the end of each peak and trough of the square wave. A description of this technique can be found at pages 219-221 of the same textbook.

[0016] Linear or cyclic voltammetry may be entirely adequate when used in this invention, but the present inventors have appreciated, as a further feature of some forms of this invention, that square wave voltammetry may be advantageous for this invention because it can observe the redox reaction of a tracer while excluding interference by other chemical species which may be present. It also provides good sensitivity and can be carried out quickly.

[0017] Examples of materials which undergo electrochemical reduction and oxidation reactions, and which may be used as tracers, include ferrocyanide ions, quinones and anthraquinones, phenylene diamine and its derivatives and ferrocene and its derivatives such as ferrocene sulfonates. Voltammetry with such compounds has been described in WO2005/066618, WO2007/034131 and references cited therein. Another category of materials which may be used as redox active tracers come from the family of purines (organic compounds with fused pyrimidine and imidazole rings) especially purines which incorporate keto groups such as xanthine. Various other organic chemicals are redox active, including oxidisable hydroxy acids such as ascorbic acid. Bromides and iodides may also be used as tracers: voltammetry with these has been described by Wu et al in J. Anal. Chem Vol 60, pp1062-1068 (2005).

[0018] Another possibility is to choose a metallic ion as tracer and estimate its concentration by means of adsorptive stripping voltammetry (ASV). In this case the metallic species is first accumulated at the electrode surface by the imposition of a reducing potential (more negative than that of the redox species of interest). The reduction process results in electrochemical-induced deposition of the analyte onto the electrode surface. The deposited analyte is then subsequently 'stripped' from the electrode surface via application of an oxidative potential (relative to the analyte species) yielding an oxidative peak wave and thus the analytical signal used to detect the species.

[0019] A further possibility for electrochemical determination of a tracer is to select as a tracer a substance which does not itself undergo electrochemical redox reaction at an electrode but instead is a substance which reacts with another compound which itself undergoes electrochemical reaction. Such coupling between a species to be determined and the electrochemistry of a mediator compound has been described in the context of the electrochemical determination of hydrogen sulfide in WO2001/063094 and WO2004/011929. Ferrocene carboxylate and sulphonate have been suggested as possible mediator compounds in *Electroanalysis* Vol 18 pp1658-63 (2006) and in *Electrochimica Acta* Vol 52 pp499-50 (2006). A number of ferrocene sulphonates for possible use in this way have been described in *Journal of Organometallic Chemistry* Vol 692 pp5173-82 (2007). What is contemplated for the present invention is to apply this approach to the determination of a compound deliberately added as a tracer rather than analytical determination of a compound which may happen to be present. Another species which can couple to electrochemical redox reactions of a mediator compound is nitrate, as for instance disclosed by Kim et al in *Biotechnology and Bioprocess Engineering* Vol 10 pages 47-51 (2005).

[0020] For carrying out electrochemical determination of the tracer an electrochemical cell may be set up with a sample of the cement slurry or the mix-water being used as the electrolyte. The electrodes for such a cell may be provided by conventional electrodes but preferably they are provided as an array of three electrodes in laminar form deposited on an insulating laminar support. Such laminar electrodes may be formed on the support by screen printing of conductive pastes, as described in WO2004/011929. For example the working

and counter electrodes could be strips containing conductive carbon while the reference electrode could be a strip containing both silver and silver chloride

[0021] An advantage of voltammetry as an analytical technique is the small size and portability of the apparatus required. Analytical determination of tracer in accordance with this invention may be carried out with a beaker or similar container to hold a sample of slurry or mix-water, a disposable three-electrode array, a potentiostat to supply the electrical potential and observe current and a computer to control operation and store and display results.

[0022] A potentiostat can be fairly small and requires electrical power as the only supply to it. The computer could be a conventional lap-top PC. It would also be possible for the potentiostat and computer to be provided as a small single-purpose battery powered handheld unit.

[0023] Cement retarder may be a material which is already used for that purpose. Some conventional cement retarders include sodium pentaborate, calcium glucoheptonate, lignosulphonate and derivatives thereof, and a combination of phosphoric acid and the pentasodium salt of ethylenediamine tetra(methylene phosphonic acid). These materials may be shipped to a rig-site as aqueous stock solutions containing between 2 and 25 wt% of the retarder. The amount of extent of dilution will depend on the requirements of the individual cementing job but it is likely that the concentration of retarder in the mix water will lie between 0.001% and 0.1% by weight. The concentration of any other additive may also lie within such a range.

[0024] It will be desirable that the amount of tracer is less than the amount of retarder, possibly no more than 10% by weight of the retarder and possibly even less than this. Consequently, the concentration of tracer in the water or cement slurry at the time of testing is likely to lie in a range from 1 micromolar up to 10 millimolar. The amount may be at least 5 or at least 10 micromolar. It may be no more than 1 millimolar or no more than 500 micromolar.

[0025] Although it is a significant objective to check the concentration of retarder, it would be possible to check one or more other concentrations (in addition or as an alternative application of this invention) For instance the retarder could incorporate a ferrocene derivative as tracer and a dispersant could incorporate xanthine as a tracer. These give voltammetric peaks at different values of applied potential and so the concentrations of both could be determined concurrently by voltammetry.

Brief Description of the Drawings

[0026] Figs 1 and 2 are schematic diagrams illustrating an embodiment of the invention; Fig 3 schematically illustrates apparatus for testing; Fig 4 shows the square wave voltammetry response of solutions of retarder with and without xanthine tracer; Fig 5 shows the square wave voltammetry response of solutions of retarder and other additives with and without t-butylferrocene sulphonate tracer; Fig 6 shows the linear voltammetry response of solutions containing ascorbic acid as tracer, and Fig 7 is a graph constructed with data from Fig 6.

Detailed Description

[0027] As shown schematically in Figure 1, retarder and other additives are made by their manufacturers at factories 10, 11. These are manufactured as stock solutions containing a predetermined concentration of the retarder or other additive. They are shipped to a well service company which holds stocks in a warehouse 12. A tracer is added to the retarder in predetermined amount by the manufacturer at its factory 10. The weight ratio of retarder to tracer is thus fixed at that point. In the warehouse 12 the service company takes a sample from each batch of retarder and analyses it in laboratory 14 as a part of routine quality control procedure. This analysis confirms the presence and concentration of the

tracer relative to the concentration of retarder. When required, the retarder and other additives are shipped to a rig-site 16 where a well has been drilled.

[0028] As shown schematically in Figure 2 the well 17 has been drilled and steel casing 18 has been placed in it. Retarder indicated by arrow R, plus other additives A1, A2 etc (eg antifoam, dispersant, and fluid-loss control additives) are mixed with water W by a mixer 20 and the thus-prepared mix-water is stored in a holding tank 21 before it is mixed with cement powder C in a second mixer 22 to form a cement slurry S which is delivered to the well 17 where the slurry is pumped down the well inside the steel casing 18 and forced back up into the annular space 24 around the casing 18 where it sets.

[0029] Samples of the mix water are taken from the tank 21 and are tested using apparatus shown in Figure 3. This consists of a hand held computer 26 connected to a hand-held potentiostat 28 which is connected to an electrode array 30 consisting of three electrodes screenprinted onto an insulating substrate as described in WO2004/011929.

[0030] This electrode array is immersed into the sample 32 of mix-water and voltammetry is carried out using the computer 26 to control operation of the potentiostat and to receive, store, process and display the results.

Example 1

[0031] To demonstrate suitable electrochemistry, square wave voltammetry was carried out on a solution simulating mix-water containing a conventional retarder sodium pentaborate.

[0032] In this example, a glassy carbon working electrode was used with a standard calomel reference electrode. Voltammetry was carried out using a potentiostat from Eco Chemie BV, Utrecht, Netherlands.

[0033] The results obtained are shown in Figure 4 where curve 40 is the response when no xanthine was added. Curve 42 is the response when xanthine was added to the solution at a concentration of 40 μ M. In the absence of xanthine no distinct redox active waves were

observed in the electrochemical potential range scanned across. The lack of electrochemical activity in the pentaborate solution provided a background response and is important when using redox active tracers to detect the cement additive. Upon the addition of xanthine to the solution, a redox peak 44 emerges at ca. +0.75 V (vs. saturated calomel electrode, SCE), consistent with the theoretical redox potential for the oxidation of xanthine.

[0034] Experiments were also carried out using lower concentrations of xanthine. These showed that the peak at ca. +0.75 V increases in intensity as the concentration of added xanthine is increased. It was apparent that the limit of detection was about 10 μ M xanthine, a sensitive limit of detection which demonstrates that this is a useful method for detecting the tracer species in retarders. It is envisaged that the concentration in the mix-water would exceed this value.

Example 2

[0035] Square wave voltammetry was also carried out on solutions containing a mixture of calcium glucoheptonate (retarder), and polynaphthalene sulphonate (dispersant). Voltammetry was carried out using a glassy carbon electrode. The tracer was *t*-butylferrocene sulfonate. The results are shown in Figure 5.

[0036] Curve 50, obtained in the absence of *t*-butylferrocene sulfonate, shows no redox waves. By contrast, in curve 52, following addition of *t*-butylferrocene sulfonate to the solution a redox peak 54 emerges at +0.35 V (vs. SCE), consistent with a 1 electron oxidation of the ferrocene species to the ferricenium ion. The well defined nature of the peak enables such a species to be used as a tracer species.

Example 3

[0037] An experiment was carried out to demonstrate the quantitative detection of ascorbic acid as a tracer in a cement retarder stock solution. Voltammetry in this experiment was carried out using a glassy carbon working electrode with a standard calomel reference electrode.

[0038] A sample of a simulated mix-water fluid was prepared that comprised a typical concentration of retarder (and associated chemical tracer) after dilution from a stock solution at the rig-site. The concentration of ascorbic acid in this simulated mix-water was 0.29 mM. A voltammetric linear scan was performed at a scan rate of 0.1 volt per second and the resulting plot of current against applied potential is shown as curve 56 in Figure 6. It is the characteristic Faradaic signal associated with the oxidation of ascorbic acid. Curve 58 is a base line curve obtained with a similar solution omitting the ascorbic acid.

[0039] A 100 mM standard solution of ascorbic acid was prepared in deionised water., 80uL aliquots of this ascorbic acid standard solution were added consecutively to the retarder solution. After each addition a voltammetric scan was carried out. The resulting curves are shown in Figure 6 and, as indicated by the vertical arrow, the presence of increasing amounts of ascorbic acid led to increasing current at +0.8volt relative to the reference electrode.

[0040] Following each of eight such separate additions, the peak height at +0.8 volt was plotted versus the *added* ascorbic acid concentration. The plot is illustrated in Figure 7. The negative intercept on the abscissa of the graph gives the ascorbic acid concentration in the simulated sample. As illustrated in Figure 7, the Y=0 value on the X-axis was at a value of -0.27 mM and therefore the concentration of ascorbic acid in the simulated sample had been determined by this simple experimental procedure to be 0.27 mM which corresponds well to the actual value of 0.29 mM.

[0041] This example has thus shown that a redox-active species (such as ascorbic acid) can usefully be used as a chemical tracer to 'tag' a cement retarder solution at a known ratio of tracer to retarder. Following dilution of the cement retarder solution, prior to mixing with cement, the concentration of the chemical tracer can be determined via a voltammetric standard addition experiment. From this, and the known ratio of tracer to retarder, the actual concentration of the retarder after dilution can be determined easily.

Claims

1. A process of preparing a settable slurry by mixing a solid powder, water and one or more additives, characterised by mixing a tracer material with an additive before mixing that additive with the solid powder and the water and analysing a mixture containing at least the additive and at least part of the water to determine the concentration of tracer therein.
2. A process according to claim 1 wherein the step of analyzing a mixture is performed on the slurry.
3. A process according to claim 1 wherein the step of analyzing a mixture is performed on a mixture of the additive and water before mixing with the solid powder.
4. A process according to claim 1 wherein the solid powder is cement, so that the slurry is a cement slurry.
5. A process according to claim 4 wherein said additive with which the tracer is mixed is a cement set retarder.
6. A process according to claim 5 which includes a step of pumping the cement slurry into a space between a borehole and a casing within the borehole.
7. A process according to claim 1 wherein the tracer is mixed with the additive at a manufacturing or storage facility and the additive with admixed tracer is subsequently transported to another site for preparing the slurry by mixing with the solid powder and water.
8. A process according to claim 1 wherein analysis to determine the concentration of tracer is carried out by electrochemistry.

9. A process according to claim 8 carried out with an array of laminar electrodes formed on an insulating substrate.
10. A process according to claim 8 wherein the tracer undergoes electrochemical oxidation and/or reduction and analysis is carried out using voltammetry to determine the concentration of tracer.
11. A process according to claim 10 where analysis is carried out using square wave voltammetry.
12. A process according to claim 8 wherein
the step of analyzing a mixture is performed on a mixture containing a mediator compound which undergoes electrochemical oxidation and reduction
the tracer undergoes chemical reaction with the mediator compound, and
analysis is carried out using voltammetry to observe the effect of tracer on electrochemical reaction of the mediator compound.

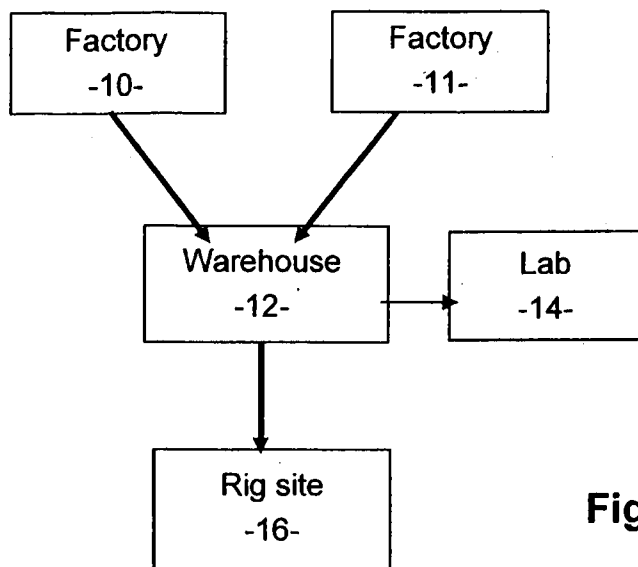


Fig 1

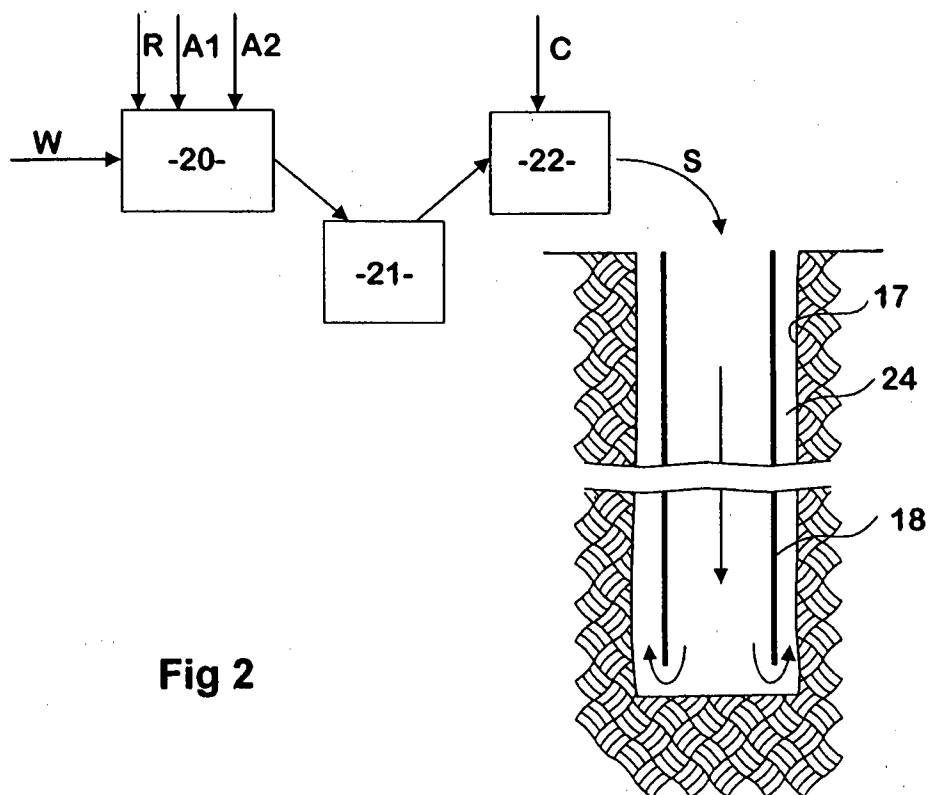
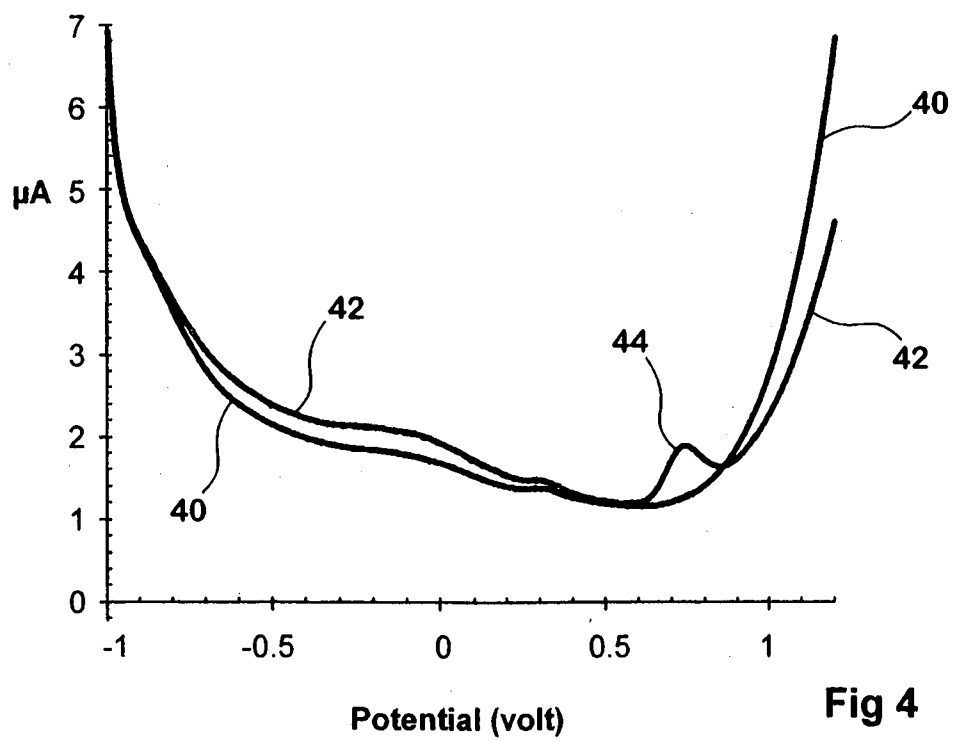
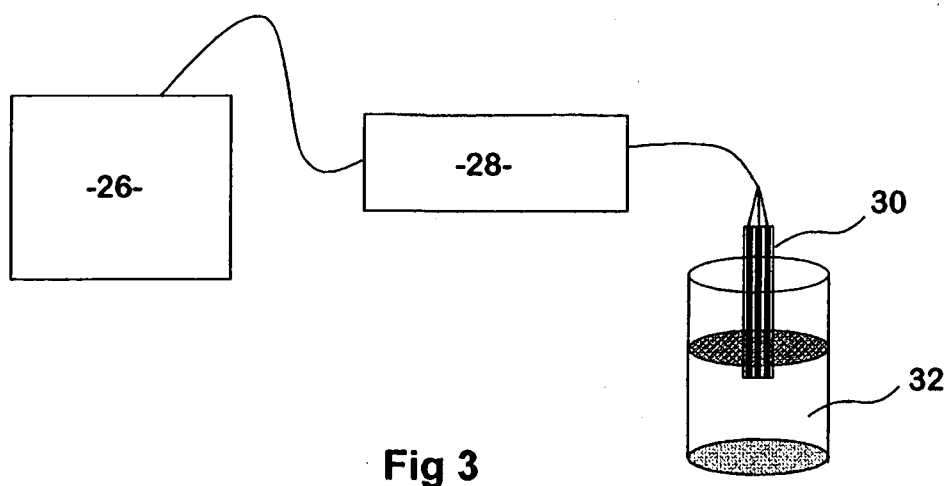


Fig 2



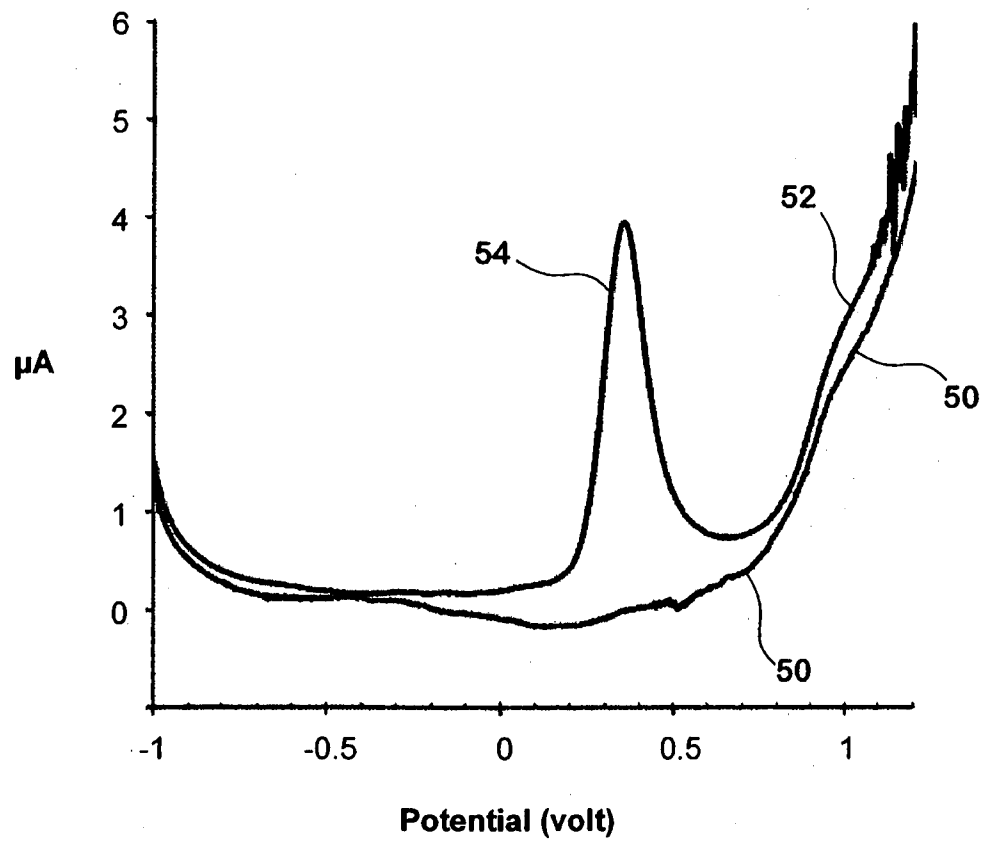


Fig 5

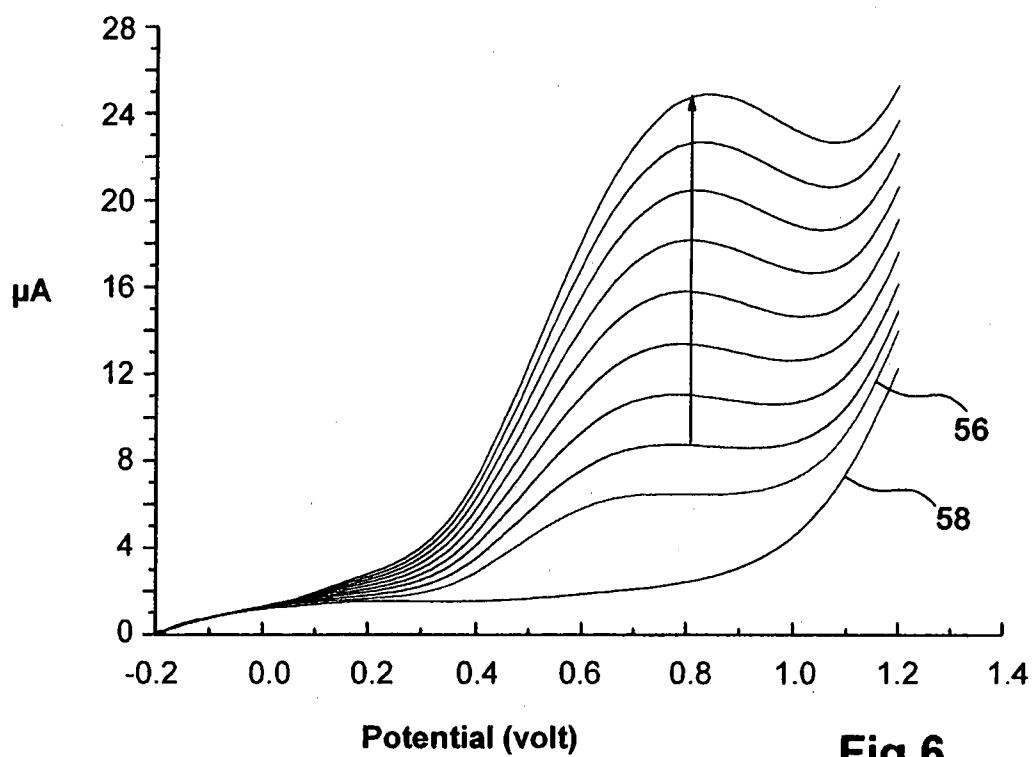


Fig 6

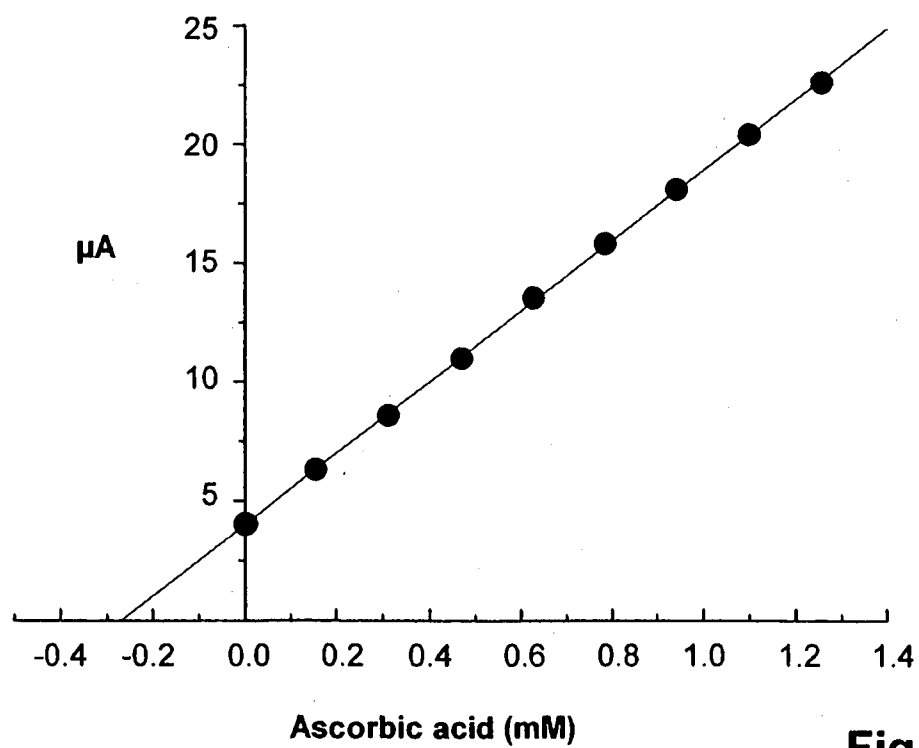


Fig 7