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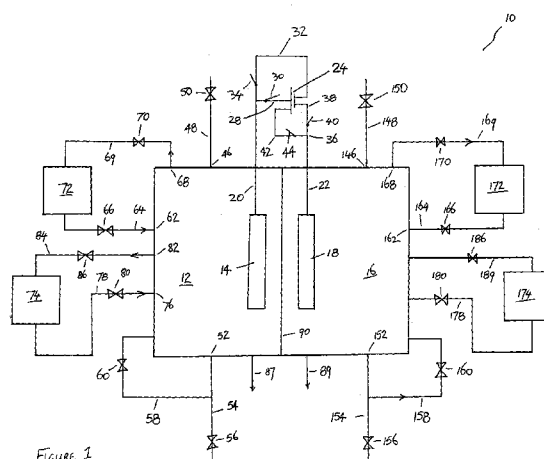


Figure 1

(57) **Abstract:** A method for treating a sulfide containing solution comprises providing an electrochemical system comprising a first electrode compartment having a first electrode and a second electrode compartment having a second electrode, supplying the first electrode compartment with the sulfide containing solution and operating the first electrode as an anode to oxidise sulfide to form elemental sulfur or other sulfur forms more oxidized than sulfide, subsequently operating the first electrode compartment as a cathode and operating the second electrode compartment as an anode such that elemental sulfur or other sulfur forms more oxidized than sulfide in the first electrode compartment is reduced to sulfide or polysulfide (or both) and feeding the sulfide containing solution to the second electrode compartment to oxidise sulfide to form elemental sulfur or other sulfur forms more oxidized than sulfide and subsequently operating the second electrode compartment as a cathode and operating the first electrode compartment as an anode such that sulfur or other sulfur forms more oxidized than sulfide in the second electrode compartment is reduced to sulfide or polysulfide (or both) and feeding the sulfide containing solution to the first electrode compartment to oxidise sulfide to form sulfur or other sulfur forms more oxidized than sulfide, wherein a cathode solution containing sulfide or polysulfide of enhanced concentration when compared to the solution fed to the anode is obtained.

TREATMENT OF SULFIDE CONTAINING MATERIAL

FIELD OF THE INVENTION

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The present invention relates to a method for treating sulfide containing solutions or liquids.

BACKGROUND TO THE INVENTION

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Sulfide is found in the environment as dissolved sulfide in wastewaters and as gaseous hydrogen sulfide in waste gases. Sewage and industrial wastewaters from sources such as petrochemical plants, tanneries, pulp and paper plants, generate significant quantities of aqueous solutions containing sulfide. Geothermal brines can contain
15 significant amounts of sulfide. Gaseous sources, such as biogas, natural gas and off-gases from wastewater treatment systems, are important sources of gaseous sulfide. Sulfide is toxic, corrosive and malodorous. Therefore, its removal from wastewaters and waste gases is required from both an environmental and economic viewpoint.

20 A variety of methods have been developed to achieve sulfide removal, such as chemical oxidation and catalytic conversion. These processes typically oxidise sulfide to either elemental sulfur or sulfate, thus achieving sulfide removal from wastewaters and waste gases. However, these methods require substantial energy and chemical inputs. Moreover, as yet, there are no processes available that can recover sulfide
25 from wastewaters for onsite reuse in other processes.

BRIEF DESCRIPTION OF THE INVENTION

The present invention relates to a method to treat a sulfide containing solution. In
30 some embodiments, the sulfide is recovered as sulfur or polysulfide (S_n^{2-}). In other embodiments, the sulfide is formed into a more concentrated sulfide solution for re-use or for more efficient sulfide treatment.

In one aspect, the present invention provides a method for treating a sulfide containing solution comprising:

- 5 a) providing an electrochemical system comprising a first electrode compartment having a first electrode and a second electrode compartment having a second electrode;
- 10 b) supplying the first electrode compartment with the sulfide containing solution and operating the first electrode as an anode to oxidise sulfide to form elemental sulfur or other sulfur forms more oxidized than sulfide;
- 15 c) subsequently operating the first electrode compartment as a cathode and operating the second electrode compartment as an anode such that elemental sulfur or other sulfur forms more oxidised than sulfide in the first electrode compartment is reduced to sulfide or polysulfide (or both) and feeding the sulfide containing solution to the second electrode compartment to oxidise sulfide to form elemental sulfur or other sulfur forms more oxidized than sulfide;
- 20 d) subsequently operating the second electrode compartment as a cathode and operating the first electrode compartment as an anode such that sulfur or other sulfur forms more oxidised than sulfide in the second electrode compartment is reduced to sulfide or polysulfide (or both) and feeding the sulfide containing solution to the first electrode compartment to oxidise sulfide to form sulfur or other sulfur forms more oxidised than sulfide;
- 25 wherein a cathode solution containing sulfide or polysulfide of enhanced concentration when compared to the solution fed to the anode is obtained.

30 In some embodiments, the method of the present invention further comprises sequentially repeating steps (c) and (d).

In some embodiments of the present invention, a relatively small volume of solution is supplied to the cathode, when compared to the volume of solution supplied to the

anode, in order to form a cathode solution containing sulfide or polysulfide of enhanced concentration when compared to the solution fed to the anode.

5 In some embodiments, the first cathode solution from the second electrode compartment could be fed back in the first electrode compartment when it is used as cathode to achieve concentrated sulfide/polysulfide solution and vice versa. This process may be continued for each cycle to ultimately provide a very concentrated polysulfide/sulfide solution or alkaline solution.

10 As electrode materials, any conductive material with sufficient stability in the used conditions can be applied. Examples of materials include plain graphite, graphite felt, graphite granules, carbon, steel, or other materials as known to a person skilled in the art. This list is not limiting.

15 For the reasons of brevity of description, throughout the remainder of this specification, operation of the anode to oxidise sulfide to elemental sulfur or other sulfur forms more oxidised than sulfide shall be referred to by the expression "oxidising sulfide to sulfur" (or similar). However, it will be understood that this expression relates to oxidising sulfide to elemental sulfur or other sulfur forms more
20 oxidised than sulfide. Similarly, reference to "sulfur" shall also be taken to be a reference to elemental sulfur or other sulfur forms more oxidised than sulfide.

In some embodiments of the present invention, the electrode that is operated as a cathode is initially provided with a first cathode solution in which sulfide or
25 polysulfide (or both) is formed, and subsequently provided with a second cathode solution and the cathode is operated such that pH of the second cathode solution increases. Suitably, the second cathode solution is provided to the cathode at or near a time when sulfur in or on the cathode has been fully reacted to form sulfide or polysulfide (or both). In this embodiment, the method can produce, as product streams
30 from the cathode, a first solution containing sulfide or polysulfide (with the sulfide preferably being of enhanced concentration relative to the concentration of the sulfide fed to the anode compartment) and a second cathode solution that has an alkaline pH. The second cathode solution may, for example, comprise a caustic soda solution or a potassium hydroxide solution or a mix thereof. The second cathode solution may have

a pH of greater than 10, more preferably greater than 11, even more preferably greater than 12, most preferably greater than 13.

In such embodiments, the pH of the first cathode solution may be greater than about 9.

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In another embodiment, the method may comprise providing an electrochemical system that includes a third electrode compartment containing a third electrode, the third electrode being operated as a cathode when reduction of sulfur to sulfide or polysulfide (or both) in the first electrode compartment or second electrode compartment is nearly or essentially complete. In this embodiment, the third electrode compartment can be used to generate the alkaline containing solution as a product stream. In this embodiment, the third electrode compartment may always operate as a cathode.

15 In yet another embodiment, the method may comprise providing an electrochemical system that includes a third electrode compartment containing a third electrode, each of the first electrode, second electrode and third electrode being sequentially operated as the anode such that sulfide in the sulfide containing solution fed to the anode is oxidised to form sulfur on the anode to thereby sequentially load the first electrode, 20 second electrode and third electrode with sulfur, subsequently operating the electrode loaded with sulfur as a cathode to form a solution containing sulfide or polysulfide (or both) whilst at the same time operating one of the other electrodes as the anode to thereby load the anode with sulfur, wherein when sulfur in the cathode is nearly or essentially exhausted, the remaining electrode is operated as a cathode to thereby 25 generate an alkaline containing solution.

In this embodiment of the present invention, one of the electrodes (which operates as the anode) is loaded with sulfur by oxidising sulfide to sulfur. That electrode is then switched to operate as the cathode so that a solution containing enhanced 30 concentration of sulfide or containing polysulfide is formed. At the same time, another of the electrodes is operated as the anode to load that electrode with sulfur. During each cycle, it is anticipated that reduction of sulfur to sulfide or polysulfide at the cathode will considerably decrease sulfur in the cathode compartment before the anode becomes fully loaded with sulfur. Therefore, when the sulfur in the cathode is

to a large extent exhausted, the remaining electrode is operated as the cathode to form an alkaline containing solution.

5 In some embodiments of the present invention, reduction of sulfur at the cathode forms a polysulfide containing solution. The polysulfide containing solution can be recovered for subsequent use. Alternatively, the polysulfide containing solution can be treated to form a sulfide containing solution of enhanced sulfide concentration when compared to the sulfide containing solution fed to the anode. As a sulfide containing solution of enhanced concentration is obtained, treatment of that stream to
10 remove sulfide is simplified. Alternatively, the polysulfide solution can be treated to form elemental sulfur. Methods to achieve this include aeration, pH correction and others as known to a person skilled in the art.

The sulfide containing solution that is fed to the anode in the present invention may
15 comprise a sulfide containing wastewater.

In another embodiment of the present invention, a sulfide containing solution may be formed in order to recover and recycle sulfide to another process that requires sulfide as a feed input.

20

In some embodiments, the liquid stream provided to the anode has a pH higher than 7. At this pH, sulfur precipitating on the anode can react with solution sulfide to form polysulfide. In order to maximize the sulfur yield, the electrochemical system can be operated sufficiently long to oxidize all sulfide and subsequently polysulfide to
25 elemental sulfur at the anode. Thus, in the absence of sulfide the sulfur on the anode becomes stabilized even at pH values higher than 7.

In some embodiments, the cathode solution of the electrochemical system is used to capture sulfide from a gaseous stream. Indeed, the consumption of protons in the
30 cathode leads to increasing pH. This allows capturing of sulfide, (for example, as is present in gaseous streams) in the cathode liquid, while simultaneously e.g. sulfur is reduced to sulfide at the cathode. Examples of such gaseous streams that contain sulfide include biogas, natural gas, flue gas, refinery gas, or any sulfide containing gaseous stream as known to a person skilled in the art. The objective of the

electrochemical system can, in these embodiments, be extended to the treatment of sulfide containing gases in conjunction with the treatment of a liquid stream that contains sulfide. Particularly in the case of anaerobic digestion, where both a biogas containing gaseous sulfide (typically hydrogen sulfide) and a liquid effluent stream
5 containing dissolved sulfide are present, this embodiment can remove sulfide from the two streams simultaneously and achieve sulfide recovery. This embodiment could be combined with a bioelectrochemical system, where a caustic solution is generated via anodic oxidation of organics (such as described in International patent application number WO2010042987 entitled "Treatment of solutions or wastewater", the entire
10 contents of which are herein incorporated by cross reference) and/or sulfide as described here.

In a further embodiment of the above, a bioelectrochemical or electrochemical system is used to capture sulfide from a gaseous stream at the cathode, after which the
15 effluent of this cathode is sent to a second electrochemical system for recovery of the sulfide in a separate stream as described earlier. The effluent of the electrochemical system, now low in sulfide, can in certain embodiments be sent back to the bioelectrochemical system for further sulfide recovery.

20 In another embodiment, the cathode of a bioelectrochemical or electrochemical system is used to capture both CO₂ and sulfide from a gaseous stream. The effluent of this cathode is sent to an electrochemical system for recovery of the sulfide via the aforementioned methods, while the CO₂ remains in the fluid or is stripped into a separate, gaseous phase. This embodiment allows removing both CO₂ and sulfide
25 from gaseous streams such as biogas, flu gas or other gaseous stream as known to a person skilled in the art.

In all embodiments of the present invention, the electrode compartments may be separated from each other by an ion permeable membrane. Suitably, the ion
30 permeable membrane allows the passage of ions therethrough. Such ion permeable membranes may include ion exchange membranes, such as cation exchange membranes, anion exchange membranes, and bipolar membranes. Porous membranes, such as microfiltration membranes (i.e., microporous polyvinylchloride), ultrafiltration membranes, and nanofiltration membranes, may also be used in the

present invention. The ion permeable membrane facilitates the transport of positively and/or negatively charged ions through the membrane, which compensates for the flow of the negatively charged electrons from anode to cathode and thus maintains electroneutrality in the system.

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In one embodiment, the ion permeable membrane may comprise a cation exchange membrane. The cation exchange membrane may allow the passage of cations from the anode to the cathode. Cation exchange membranes are known to the person skilled in the art and include membranes such as CMI-7000 (Membranes International),
10 Neosepta CMX (ASTOM Corporation), fumasep® FKB (Fumatech), and Nafion (DuPont).

In another embodiment of the invention the ion permeable membrane that separates the anode and the cathode chamber comprises an anion exchange membrane. Anion
15 exchange membranes are known to the person skilled in the art and include membranes such as AMI-7001 (Membranes International), Neosepta AMX (ASTOM Corporation), and fumasep FAA® (fumatech). In cases where an anion exchange membrane is used as the membrane in the system, anions are transported from the cathode to the anode to compensate for the negative charge of the electrons flowing
20 from anode to cathode through the electrical circuit. As cations are blocked completely by the anion exchange membrane, multivalent cations cannot be transported from anode to cathode and scaling issues are prevented.

In another embodiment of the invention the ion permeable membrane that separates
25 the anode and the cathode chamber comprises a bipolar membrane. Bipolar membranes are known to the person skilled in the art and include membranes such as NEOSEPTA BP-1E (ASTOM Corporation) and fumasep® FBM (Fumasep). Bipolar membranes are composed of a cation exchange layer on top of an anion exchange layer and rely on the principle of water splitting into protons and hydroxyl ions in
30 between the ion exchange layers of the membrane, according to:



In cases where a bipolar membrane is used as the membrane in the system, the anion exchange layer is directed towards the anode chamber and the cation exchange layer is directed towards the cathode chamber. When electrical current flows, water diffuses in between the ion exchange layers and is split into protons and hydroxyl ions. The hydroxyl ions migrate through the anion exchange layer into the anode chamber, where they compensate for the proton production in the anode reaction and the protons migrate through the cation exchange layer into the cathode chamber where they compensate for the hydroxyl ion production (or proton consumption) in the cathode reaction. As a result of this, pH may be kept constant in the cathode chamber without adding acid. Furthermore, because other anions and cations are not transported through the bipolar membrane, multivalent cations cannot be transported from anode to cathode either and scaling issues are prevented.

The present invention also encompasses electrochemical systems suitable for use in the methods described above.

Accordingly, in another aspect, the present invention provides an electrochemical system comprising a first electrode compartment having a first electrode, a second electrode compartment having a second electrode and a third electrode compartment having a third electrode, the first electrode compartment being provided with an anode solution inlet for supplying an anode solution thereto and cathode solution inlet for supplying a first cathode solution thereto, the second electrode compartment being provided with anode solution inlet for supplying an anode solution thereto and cathode solution inlet for supplying a first cathode solution thereto, the third electrode compartment being provided with a second cathode solution inlet for supplying a second cathode solution thereto.

In this aspect of the present invention, the first electrode and the second electrode may be arranged such that the first electrode sequentially operates as an anode and a cathode and the second electrode sequentially operates as a cathode and an anode, with the third electrode operating as a cathode.

In a further aspect, the present invention provides an electrochemical system comprising a first electrode compartment having a first electrode, a second electrode compartment having a second electrode and a third electrode compartment having a third electrode, the first electrode compartment being provided with anode solution inlet for supplying an anode solution thereto and at least one cathode solution inlet for supplying a first cathode solution thereto and for supplying a second cathode solution thereto, the second electrode compartment being provided with an anode solution inlet for supplying an anode solution thereto and at least one cathode solution inlet for supplying a first cathode solution thereto and for supplying a second cathode solution thereto and the third electrode compartment being provided with anode solution inlet for supplying an anode solution thereto and at least one cathode solution inlet for supplying a first cathode solution thereto and for supplying a second cathode solution thereto.

In this aspect of the present invention, the first electrode, the second electrode and the third electrode may be electrically connected such that one of the electrodes is operated as an anode, another of the electrodes is operated as a first cathode to reduce sulfur on that cathode and the other of the electrodes is operated as a second cathode to form an alkaline solution when sulfur on the other cathode is exhausted, and the first electrode, second electrode and third electrode each sequentially operate as the anode, the first cathode and the second cathode.

The electrochemical system used in the present invention will be provided with appropriate electrical switching in order to allow the electrodes to be switched between anodic and cathodic operation. The electrochemical system used in the present invention will also be provided with appropriate valving on all influent lines and effluent lines to control the flow of liquid to and from the respective electrode compartments and to ensure that the desired liquid is provided at the desired time to the desired electrode compartment. The electrochemical system may have an appropriate control system to ensure that proper electrical switching and operation of the valving takes place. The person skilled in the art will really appreciate that a number of different control systems may be implemented to achieve the desired control outcome.

As mentioned above, the present invention may be used to form a sulfide containing solution in order to recover and recycle sulfide to another process that requires sulfide as a feed input. One example of such a process involves the removal of phosphate from an aqueous solution, such as a wastewater stream. Phosphate removal is essential from wastewater since any additional discharge of phosphorus to waterways contributes to eutrophication (algal growth). Removal of phosphate is also an essential pre-treatment in reverse osmosis-based water recycling processes to avoid precipitation/scaling in the reverse osmosis modules. Known processes for removing phosphate from aqueous solutions involve adding metal ions, frequently ferric ions (Fe(III), usually in the form of ferric chloride or ferric sulfate), to the aqueous solution to form metal phosphate precipitates. The metal phosphate precipitates can then be separated from the liquid as a sludge. Addition of metal ions, such as ferric ions, and handling of metal phosphate sludge are associated with significant operational costs in wastewater treatment processes.

Therefore, in a further aspect, the present invention provides a method for treating a metal phosphate containing material, such as a metal phosphate containing sludge, comprising the steps of adding sulfide to the metal phosphate containing material to form metal sulfide precipitates whilst releasing phosphate into solution, separating a phosphate containing solution from the metal sulfide precipitates, feeding the metal sulfide precipitates to an electrochemical system comprising a first electrode compartment having a first electrode and a second electrode compartment having a second electrode, supplying the first electrode compartment with metal sulfide and operating the first electrode as an anode to oxidise metal sulfide to form sulfur or another form of sulfur that is more oxidised than sulfide and metal ions, subsequently operating the first electrode compartment as a cathode and operating the second electrode compartment as an anode such that sulfur or another form of sulfur that is more oxidised than sulfide in the first electrode compartment is reduced to sulfide or polysulfide (or both) and supplying the second electrode compartment with the metal sulfide to oxidise sulfide to form sulfur, recovering a sulfide containing solution from the electrode compartment that is operating as a cathode and returning the sulfide containing solution to be mixed with the metal phosphate containing sludge.

In embodiments of this aspect of the present invention, the metal sulfide may comprise a sulfide containing iron, arsenic, aluminium, cobalt, copper, nickel, silver, cadmium, barium, calcium, manganese, mercury, lead, zinc, magnesium or other metals as known to a person skilled in the art, or mixtures of two or more thereof.

5 These metals can originate from aqueous streams containing dissolved metals.

In one embodiment, the metal phosphate containing material is an iron phosphate sludge. In this embodiment, the method comprises treating an iron phosphate containing sludge comprising the steps of adding sulfide to the iron phosphate
10 containing sludge to form iron sulfide precipitates whilst releasing phosphate into solution, separating a phosphate containing solution from the iron sulfide precipitates, feeding an aqueous mixture containing the iron sulfide precipitates to an electrochemical system comprising a first electrode compartment having a first electrode and a second electrode compartment having a second electrode, supplying
15 the first electrode compartment with the iron sulfide containing aqueous mixture and operating the first electrode as an anode to oxidise iron sulfide to form sulfur or another form of sulfur that is more oxidised than sulfide and ferric (Fe(III)) or ferrous (Fe(II)) ions (or both), subsequently operating the first electrode compartment as a cathode and operating the second electrode compartment as an anode such that sulfur
20 or another form of sulfur that is more oxidised than sulfide in the first electrode compartment is reduced to sulfide or polysulfide (or both) and supplying the second electrode compartment with the iron sulfide to oxidise sulfide to form sulfur or another form of sulfur that is more oxidised than sulfide, recovering a sulfide containing solution from the electrode compartment that is operating as a cathode and
25 returning the sulfide containing solution to be mixed with the iron phosphate containing sludge.

Suitably, the iron phosphate containing sludge is formed by mixing a solution containing ferric or ferrous ions (or both) with a solution containing dissolved
30 phosphate and a solution containing ferric or ferrous ions (or both) is recovered from the electrode compartment operating as the anode and the solution containing ferric or ferrous ions (or both) is returned to be mixed with the solution containing dissolved phosphate to form further iron phosphate containing sludge.

This aspect of the present invention treats an iron phosphate containing sludge to recover and reuse sulfide in the treatment of the iron phosphate containing sludge. Advantageously, this method may also recover and return a solution containing ferric or ferrous ions (or both) in the treatment of solutions containing dissolved phosphate to form further iron phosphate containing sludge. Accordingly, the input requirements of both sulfide and ferric or ferrous (or both) solution will be reduced.

The sulfide recovery step in this method may utilise a method similar to the method as described in the first aspect of the present invention. This method involves operating one of the electrode compartments as an anode to form elemental sulfur on the anode whilst, at the same time, operating the other electrode compartment as a cathode so that elemental sulfur deposited on that electrode is reduced to sulfide or polysulfide (with the polysulfide subsequently being transformed into sulfide). Once the anode is loaded with elemental sulfur, the anode and cathode are switched so that the electrode loaded with elemental sulfur becomes the cathode and the elemental sulfur on the cathode is reduced to polysulfide and sulfide. The switching suitably happens periodically. The cathode compartment may be operated for part of the cathode cycle to recover a sulfide containing solution and for a later part of the cathode cycle to recover an alkaline solution when the elemental sulfur on the cathode has been exhausted. This aspect of the present invention may also utilise a third electrode compartment, as described above.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic diagram of an electrochemical apparatus suitable for use in an embodiment of the present invention;

Figure 2 shows a schematic diagram of the apparatus shown in figure 1 in which the first electrode is operating as an anode and the second electrode is operating as a cathode for the production of sulfide or polysulfide;

Figure 3 shows a schematic diagram of the apparatus shown in figure 1 in which the first electrode is operating as an anode and the second electrode is operating as a cathode for the production of an alkaline solution;

Figure 4 shows a schematic diagram of the apparatus shown in figure 1 in which the second electrode is operating as an anode and the first electrode is operating as a cathode for the production of sulfide or polysulfide;

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Figure 5 shows a schematic diagram of the apparatus shown in figure 1 in which the second electrode is operating as an anode and the first electrode is operating as a cathode for the production of an alkaline solution;

10 Figure 6 shows a schematic diagram of one embodiment of a three electrode chamber electrochemical apparatus suitable for use in the present invention;

Figure 7 shows a schematic plan view of another embodiment of a three electrode chamber electrochemical apparatus suitable for use in the present invention;

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Figure 8 shows a schematic block diagram for a sulfide recovery process from ferric phosphate sludge in accordance with an embodiment of the present invention

Figure 9 shows a graph of percentage removal of sulfide and obtained current when
20 the reactor operated continuously with the effluent of an anaerobic treatment process at a flow rate of 8 L day^{-1} at controlled anode potential of $+0.2\text{V vs SHE}$ (inlet sulfide concentration $44 \pm 7 \text{ mg-S L}^{-1}$, sulfide loading rate $1.05 \pm 0.18 \text{ kg-S m}^{-3} \text{ of TAC d}^{-1}$);

Figure 10 shows SEM images of carbon fiber electrodes collected from the anode
25 chamber after 18 days operated continuously for electrochemical sulfide removal. (A) Overall view of fibres at low resolution (450X magnification) shows the presence of particulates (B) evidence of biofilm formation (8,000X magnification) (C) image used for EDS spectrum (1,600X magnification) (D) EDS spectrum of the position indicated by the cross in the centre of Fig 2C;

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Figure 11 shows a graph of percentage Sulfide-S removal, influent and effluent sulfide-S concentrations when the reactor operated continuously with periodic switching between side 1 and side 2 (anode and cathode) every 24 hours at controlled

anode potential of +0.2V vs SHE (sulfide loading rate $1.05 \pm 0.18 \text{ kg-S m}^{-3}$ of TAC d^{-1});

5 Figure 12 shows (A) SEM image (2,000X magnification) of elemental sulfur recovered from wastewater by periodic switching between anode and cathode and (B) corresponding EDS spectrum at the position indicated by the cross in Fig 11A; and

10 Figure 13 shows graphs of (A) Influent and effluent sulfide-S concentration and (B) obtained current at different loading rates for carbon fibres and graphite granules electrodes during continuous electrochemical sulfide removal at controlled anode potential of +0.2 V vs. SHE. (●) influent sulfide-S, (□) graphite granules - effluent sulfide-S and current, (▲) carbon fibres - effluent sulfide-S and current (TAC - total anodic compartment).

15 DETAILED DESCRIPTION OF THE DRAWINGS

It will be understood that the drawings have been provided for the purpose of illustrating preferred embodiments of the present invention. Therefore, it is to be understood that the present invention should not be considered to be limited solely to the features as shown in the attached drawings.

Figure 1 shows a schematic diagram of an electrochemical apparatus suitable for use in an embodiment of the present invention. Figure 1 particularly relates to an electrochemical apparatus that utilises two electrode chambers.

25 The apparatus 10 of figure 1 includes a housing or vessel 11. The apparatus 10 further comprises a first electrode chamber 12 containing a first electrode 14. The apparatus also includes a second electrode chamber 16 having a second electrode 18. The first electrode 14 and the second electrode 18 may be made from any material suitable for making electrodes for use in electrochemical systems. For example, the electrode may be made from graphite, carbon fibres, carbon based material or indeed any other suitable electrode material. Electrical wiring 20 is connected to the first electrode 14. Electrical wiring 22 is connected to the second electrode 18. A source of electricity,

such as a DC power supply 24, is connected to the wiring 20, 22. As can be seen from figure 1, wire 20 has a junction 26. Wire 28 extends from junction 26 to a positive pole of the DC power supply 24. Electrical switch 30 is positioned in wire 28 between junction 26 and the positive pole of DC power supply 24. Similarly, wire 32 extends from junction 26 to the negative pole of DC power supply 24. Electrical switch 34 is positioned in wire 32 between junction 26 and the negative pole of the DC power supply 24.

Similarly, wire 22 has a junction 36. Wire 38 having a switch 40 extends from the junction 36 to the negative pole of DC current supply 24. Wire 42 having a switch 44 extends from the junction 36 to the positive pole of the DC power supply 24.

The first electrode chamber 12 includes a wastewater inlet 46 that is connected to a wastewater feed line 48. Wastewater feed line 48 includes a valve 50. The first electrode chamber 12 also includes a wastewater outlet 52 in fluid connection with a wastewater outlet line 54. A valve 56 is provided in wastewater outlet line 54. A wastewater recycling line 58 having a valve 60 is provided to return or recycle part of the outlet wastewater from the first electrode chamber 12 back to the first electrode chamber 12. This is useful if it is desirable or necessary to recycle or return part or all of the wastewater passing through the first electrode chamber in order to obtain a lower level of sulfide in the treated waste water leaving the first electrode chamber 12.

The first electrode chamber 12 maybe operated as an anode chamber or as a cathode chamber. When first electrode chamber 12 is operated as an anode chamber, wastewater is fed to the first electrode chamber 12. However, when the first electrode chamber 12 is operated as a cathode, a cathode solution is fed to the first electrode chamber 12. In the embodiment shown in figure 1, two separate cathode solutions may be provided to the first electrode chamber 12.

In order to provide the first cathode solution to the first electrode chamber 12, the first electrode chamber 12 is provided with a first cathode solution inlet 62 that is in fluid communication with first cathode solution feed line 64. A valve 66 is provided in first cathode solution feed line 64. The first electrode chamber 12 is also provided with a first cathode solution outlet 68 that is provided with a valve 70. A first cathode

solution vessel 72 is in fluid communication with the first cathode solution inlet 62 and first cathode solution outlet line 69.

5 In order to supply a second cathode solution to the first electrode compartment 12, a second cathode solution vessel 74 is provided. The first electrode compartment 12 has a second cathode solution inlet 76 that is in fluid communication with second cathode solution feed line 78. Line 78 is provided with a valve 80. The first electrode compartment 12 also has a second cathode solution outlet 82 that is in fluid communication with the second cathode solution outlet line 84. Line 84 is provided
10 with a valve 86.

It is noted that the first cathode solution and the second cathode solution are likely to be aqueous solutions. The cathode solutions should have sufficient conductivity to allow them to function as catholytes.

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The second electrode compartment 16 may also be operated as an anode or a cathode. In order to provide the appropriate solutions to the second electrode compartment 16 at the desired times, a similar arrangement of liquid feed lines and inlets and liquid feed lines and outlets as provided to the first electrode compartment 12 is also
20 provided to the second electrode compartment 16. For convenience, the feed lines and outlet lines for the respective solutions in the second electrode compartment 16 are designated by the same reference numeral as the similar feed lines and outlet lines to the first electrode chamber 12, except that the numeral "1" has been added to the front of the reference numbers. For example, the wastewater feed line to the second
25 electrode chamber 16 is designated by reference numeral 148 (the corresponding wastewater feed line to the first electrode chamber 12 is designated by reference numeral 48). For convenience and brevity of description, these features will not be described further.

30 It will be understood that as oxidation is taking place at the anode, electrons will travel from the anode to the cathode. In order to balance the charge and to maintain an electrical circuit, an ion permeable membrane 90 is used to separate the first electrode compartment 12 from the second electrode compartment 16. The ion permeable membrane 90 may comprise a cation exchange membrane.

The apparatus 10 shown in figure 1 is operated such that the first electrode 14 operates as an anode whilst a sulfide containing wastewater is supplied to the first electrode compartment 12. At the same time, the second electrode 18 is operated as a cathode. At the anode, sulfide present in the wastewater is oxidised to elemental sulfur and elemental sulfur is deposited or coated onto the first electrode 14. When the first electrode 14 becomes fully loaded with elemental sulfur, the anode and the cathode are switched by appropriate control and operation of the electrical switches. At this time, the first electrode compartment becomes the cathode compartment and the second electrode compartment becomes the anode compartment. At the same time, the supply of wastewater to the first electrode compartment is stopped and a cathode solution is supplied to the first electrode compartment. Similarly, the supply of cathode solution to the second anode compartment is stopped and the wastewater containing sulfide is supplied to the second anode compartment.

As the first electrode, which was loaded with elemental sulfur when being operated as an anode, is now being operated as a cathode, the elemental sulfur deposited thereon becomes oxidised to polysulfide and/or sulfide. This removes elemental sulfur from the first electrode and also results in the formation of a cathode solution containing polysulfide or sulfide (or both). Desirably, the first cathode solution that is provided to the first electrode compartment is of limited volume or is recycled to the first cathode compartment many times in order to form a first cathode solution that has enhanced concentration of polysulfide or sulfide. This will allow the first cathode solution to be used in other uses that may require polysulfide or sulfide (it being appreciated that solutions of higher sulfide or polysulfide concentration are typically desirable in such instances). Alternatively if it is desired to treat the sulfide containing first cathode solution to remove sulfide therefrom using other treatments, it will be appreciated that the other treatments will become more technically and economically feasible due to the increased concentration of sulfide and the need to treat a significantly smaller volume of solution than if it was the wastewater itself (which will typically have a dilute concentration of sulfide) being treated.

As the cathode reactions typically involve the chemical production of polysulfide along with the electrochemical production of sulfide, followed by conversion of the

polysulfide in solution to sulfide, it is likely that the elemental sulfur present on the cathode will be exhausted before the anode becomes fully loaded with elemental sulfur. Therefore, during the cathode cycle, it is desirable to initially feed the first cathode solution to the cathode compartment to form the sulfide or polysulfide containing solution. When the elemental sulfur on the cathode is exhausted, the flow of first cathode solution to the cathode compartment is stopped. Recovery of fluid from each compartment may be achieved by providing drain lines 87, 89 having appropriate control valves and down stream piping (not shown). After recovery of the fluid a second cathode solution is then fed to the cathode compartment. This may require a temporary pause in the electrochemical process. The second cathode solution may be a sodium chloride solution, for example. When the elemental sulfur on the cathode is exhausted, the cathodic reaction shifts from forming polysulfide/sulfide to hydrogen evolution. This consumes protons in the second cathode solution and, as a result, the pH of the second cathode solution increases (it will also be appreciated that the cathode reaction that results in the formation of sulfur/polysulfide will also cause an increase in the pH of the first cathode solution due to hydroxide ion (OH^-) generation from the reaction). Therefore, an alkaline solution can be generated in the later part of the cathode cycle. The alkaline solution may be recovered and used in other uses. Advantageously, as the pH increases, biofilm formation on the electrode is inhibited or prevented. This addresses one of significant hurdles associated with treating wastewaters with electrochemical apparatus, that being the growth of inhibitory biofilms on the electrodes. The regular cycling of the electrodes between anode and cathode and the formation of an alkaline solution of high pH in the later part of the cathode cycle inhibits biofilm formation.

Figure 2 shows a schematic diagram of the apparatus shown in figure 1 in which the first electrode is operating as an anode and the second electrode is operating as a cathode for the production of sulfide or polysulfide. For clarity purposes, it is only the active solution lines and electrical lines that are shown in figure 2. The electrical lines that have no current flowing therethrough have been omitted from figure 2. Similarly, the solution lines that have no solution flowing therethrough have also been omitted from figure 2. Valves and electrical switches have also been omitted from figure 2. Figures 3, 4 and 5 omit similar details.

In the embodiment shown in figure 2, wastewater is being supplied to first electrode compartment 12 via wastewater feed line 48. Treated waste water is being removed from first electrode compartment 12 by wastewater outlet line 54. Wastewater recycle line 58 recycles part of the waste water back to the first electrode compartment 12. As wastewater is being fed to the first electrode compartment 12, valves 66, 70, 80 and 86 as shown in figure 1 are closed.

The first electrode compartment 12 shown in figure 2 is being used as an anode. Therefore, electrode 14 is connected via wire 22 to the positive pole of DC power supply 24. It will be appreciated that switch 30 shown in figure 1 is closed and switched 34 shown in figure 1 is open

The second electrode chamber 16 shown in figure 2 is being operated as a cathode for the production of sulfide or polysulfide. To achieve this, a first cathode solution is being fed from the vessel 172 via in line 164 to second electrode compartment 16. The first cathode solution is removed from the second cathode compartment 16 via line 169. It will be appreciated that valves 150, 156, 160, 180 and 186 as shown in figure 1 are closed.

The second electrode compartment 16 shown in figure 2 is being used as a cathode. Therefore, electrode 18 is connected via wire 22 to the negative pole of DC power supply 24. It will be appreciated that switch 40 shown in figure 1 is closed and switch 44 shown in figure 1 is open.

In operation of the apparatus 10 as shown in figure 2, the sulfide containing wastewater is fed to the anode compartment 12. The sulfide is oxidised at the anode and elemental sulfur is formed and deposited on the anode. It will be appreciated that the cathode 18 had previously been operated as an anode and accordingly it will have elemental sulfur deposited thereon. When the electrode 18 is operated as a cathode, the elemental sulfur that is deposited on the cathode 18 is reduced to form either polysulfide (S_n^{2-}) or sulfide. As polysulfide is typically formed, the elemental sulfur present on the cathode 18 becomes exhausted more quickly than the anode 14 becomes coated with elemental sulfur. At this time, the flow of first cathode solution to the cathode compartment 16 is stopped and the flow of the second cathode solution

to the cathode compartment 16 is commenced. In practice, this is achieved by closing valves 166, 170 and opening valves 180, 186. The flows of solution actually taking place at this stage are shown schematically in figure 3.

5 As shown in figure 3, the second cathode solution is supplied from vessel 174 via second cathode solution feed line 178 to second electrode compartment 16. Second cathode solution is returned from electrode compartment 16 back to vessel 174 via line 184. This second cathode solution may comprise, for example, a sodium chloride solution or other solution having sufficient conductivity to function as a catholyte.

10 Due to the reactions taking place at the cathode 18 (in the absence of elemental sulfur), the pH of the second cathode solution increases. This results in the formation of an alkaline solution. The alkaline solution may be useful in other areas, such as in the cleaning of vessels or suitable for use in other processes taking place nearby. Advantageously, the high pH that is formed in the cathode compartment in the later

15 part of the cathode cycle inhibits or prevents the formation of biofilm development on the cathode 18. It is also possible that high pH could also be obtained in the earlier part of the cathodic reaction, which may also inhibit microbial activity. It is believed that this will address one of the major hurdles associated with electrochemical treatment of wastewaters, that being the generation or formation of inhibitory biofilm

20 on the electrode surfaces to which the wastewater is fed. Biofilms are expected to either prevent the formation of elemental sulfur on the anode electrode or, if elemental sulfur is formed, in the presence of organics microorganisms in the biofilm are likely to reduce the elemental sulfur back to sulfide in the anode compartment. In either event, the net removal of sulfide from the wastewater is greatly reduced.

25 When the first electrode 14 becomes coated or fully loaded with elemental sulfur, the polarity of the electrode is switched so that the anode becomes the cathode and the cathode becomes the anode. This is achieved by an appropriate operation of the electrical switches. When switching takes place, the apparatus changes from the

30 operation are shown in figure 3 to the operation as shown in figure 4.

In figure 4, the second electrode compartment 16 operates as the anode compartment and the first electrode compartment 12 operates as the cathode compartment. To achieve this, the electrical switches are operated such that second electrode 18 is

connected to the positive pole of the DC power supply 24 and the first electrode 14 is connected to the negative pole of the DC power supply 24. At the same time, the valves in the second electrode compartment 16 operated such that the sulfide containing wastewater is fed to the second electrode compartment 16 via line 148 and removed via line 154. Recycle, if required, is achieved via line 158. It will be appreciated that the valves 166, 170, 180 and 186 are closed.

The first electrode compartment 12 is now operating as the cathode in the early part of the cathode cycle. Therefore, the first electrode 14 (which is now operating as a cathode) is loaded with elemental sulfur and the cathode reactions result in the formation of polysulfide and/or sulfide. A first cathode solution is fed from vessel 72 via line 64 to the first electrode compartment 12. The first cathode solution is returned from the first electrode compartment 12 back to the vessel 72 via line 69. As a result of this, the polysulfide/sulfide concentration of the first cathode solution 72 increases.

When the sulfur on the first electrode 14 is exhausted, the flow of first cathode solution to the first electrode compartment 12 is stopped and the flow of second cathode solution to the first electrode compartment 12 commences. This is shown schematically in figure 5. During this stage of the cycle, the pH of the second cathode solution increases. Elemental sulfur continues to be deposited on the anode. In some embodiments, if it is desired to form a sulfide solution in the first cathode, the first cathode may continue to operate until both sulfur and polysulfide are exhausted (polysulfide that is formed will then also be reduced to sulfide).

When the second electrode is fully loaded with elemental sulfur, the anode in the cathode are again switched and operation reverts back to that as shown in figure 2. The method then cycles through the operations shown respectively in figures 3, 4 and 5 and then back to figure 2.

It will be appreciated that in some embodiments, only a single cathode solution is used. If that occurs, the cycle of steps that the process utilises are as shown in figure 2, then in figure 4, then back to figure 2, etc. In this embodiment, the pH of the sulfide containing cathode solution also increases.

At various times, the cathode solutions may be removed from their respective vessels and used in alternative uses. When that occurs, fresh cathode solutions may be provided to the respective cathode vessels. The respective cathode vessels may be provided with appropriate outlets and withdrawal lines to withdraw cathode solution
5 from the vessels.

Figure 6 shows a schematic diagram of an apparatus in accordance with another embodiment of the present invention. In figure 6, the apparatus 200 comprises a first electrode compartment 210 having a first electrode 212, a second electrode
10 compartment 214 having a second electrode 216, and a third electrode compartment 218 having a third electrode 220. The first electrode compartment 210 and the second electrode compartment 214 may be switched between operation as cathode and anode. The third electrode compartment 220 always operates as a cathode. For clarity and brevity of description, solution feed lines, solution removal lines and electrical wiring
15 and switching have been largely omitted from figure 6.

In operation of the apparatus shown in figure 6, the first electrode 212 is operated as an anode. Sulfide containing wastewater is fed to the first electrode compartment 212. The second electrode 216, which is initially loaded with elemental sulfur during the
20 early stages of the cathode cycle, is operated as a cathode. This results in the formation of a cathode solution containing polysulfide and/or sulfide. At this stage, the third electrode 220 is not connected to an electrical power source.

When the second electrode 216 becomes exhausted in elemental sulfur (or both
25 elemental sulfur and polysulfide), power to the second electrode 216 is switched off and power to the third electrode 220 is switched on such that the third electrode 220 now acts as a cathode (at this stage, first electrode 212 is still operating as an anode). This results in the formation of an alkaline solution in the third electrode compartment 218.

30 The apparatus shown in figure 6 includes a DC power supply 222, electrical wires 224 and 226 that connect the first and second electrodes to the DC power supply 222 and a third electrical wire 228 that connects the third electrode 222 to the DC power supply 222. Switch 230 is used to selectively isolate and connect the second anode 216 to the

DC power supply 222. Switch 232 is used to selectively isolate the third electrode 222 from the DC power supply 222. It will be appreciated that additional wiring and electrical switches (not shown) will be used to achieve the desired electrical connections when the first anode 212 and second anode 216 are switched to operate
5 from anode to cathode and vice versa.

The apparatus 200 shown in figure 6 also includes cation exchange membranes 234 that separate the first and second electrode compartments and 236 that separates the third electrode compartment from both the first electrode compartment and the second
10 electrode compartment.

Figure 7 shows a schematic plain view of another apparatus suitable for use in the present invention. In figure 7, the apparatus 300 includes a first electrode compartment 302 having a first electrode 304, a second electrode compartment 306
15 having a second electrode 308 and a third electrode compartment 310 having a third electrode 312. A cation exchange membrane 314 separates the first electrode compartment 302 from the second electrode compartment 306. A cation exchange membrane 316 separates the second electrode compartment 306 from the third electrode compartment 310. A cation exchange membrane 318 separates the third
20 electrode compartment from the first electrode compartment.

In operation of the apparatus shown in figure 7, each of the first electrode, second electrode and third electrode are sequentially and periodically operated as the anode. For example, the first electrode 304 is operated as the anode and becomes loaded with
25 elemental sulfur. When it is fully loaded with elemental sulfur, the second electrode 308 becomes the anode and the first electrode 304 becomes the cathode. As the cathode 304 is loaded with elemental sulfur, sulfide/polysulfide is formed by the cathode reactions in the first electrode compartment 302.

30 When cathode 304 becomes depleted of elemental sulfur (or elemental sulfur and polysulfide), the power supply to cathode 304 is interrupted and third electrode 312 is connected to the power supply such that third electrode 312 now operates as the cathode. At this time, second electrode 308 is still acting as the anode, with sulfide containing wastewater being fed to second electrode compartment 306. Therefore, at

this stage, second electrode 308 operates as the anode and elemental sulfur continues to be deposited thereon. The third electrode 312 is now acting as a cathode and an alkaline solution is being generated in third electrode compartment 310. First electrode 304 has no power supply to it and it is essentially inactive.

5

When second electrode 308 is fully loaded with sulfur, the electrical connections are altered such that second electrode 308 becomes the cathode and third electrode 312 becomes the anode. Wastewater is supplied to the third electrode 312 and the anode reactions result in the oxidation of sulfide to form elemental sulfur on the third electrode 312. Sulfide/polysulfide is formed by the cathode reactions at second electrode 308. When the second electrode 308 becomes depleted in elemental sulfur (or elemental sulfur and polysulfide), the electrical connections are switched and the second electrode trigger an eight becomes largely inactive and the first electrode 304 becomes the cathode to thereby form an alkaline solution in the first and own compartment 302.

15

The cycle can then continue around the apparatus.

As an alternative, instead of the apparatus shown in figure 7 having each of the three electrodes being used as the anode and a cathode, only two of those electrodes may switch between use as the anode and a cathode, with the third (or the remaining) electrode always operating as a cathode when the cathode cycle reaches the stage where elemental sulfur (or elemental sulfur and polysulfide) on the other cathode is depleted.

25

Figure 8 shows a schematic flow sheet of a process for treating ferric phosphate sludge with recovery of both Fe(III) and sulfide. In the flow sheet shown in figure 8, a ferric phosphate sludge 400 is contacted with a sulfide 402. The ferric phosphate sludge may be formed by contacting a wastewater containing dissolved phosphates with a solution containing dissolved ferric ions, which will typically be ferric chloride solution.

30

The sulfide that is contacted with the ferric phosphate sludge may be hydrogen sulfide (in aqueous solution) or a polysulfide solution. This causes the precipitation of black

iron sulfides (FeS , FeS_2 , Fe_2S_3) and releases phosphate back into solution. As the ferric phosphate sludge constitutes a relatively concentrated phosphate source, the phosphate that is released into solution is of a relatively high concentration. The mixture of iron sulfide sludge and phosphate solution is separated at 404 and the phosphate solution 406 is removed. The iron sulfide sludge 408 is passed to electrochemical cell 410. Electrochemical cell 410 may be similar to any of the cells shown in figures 1 to 7. At the anode, the iron sulfides are oxidised to form elemental sulfur on the anode. Once the anode is fully loaded with elemental sulfur, the anode and cathode are switched and elemental sulfur starts to become deposited on the new anode. At the new cathode (which, at this stage, is still loaded with elemental sulfur), reduction of the elemental sulfur to sulfide/polysulfide occurs. The sulfide/polysulfide containing solution formed in the cathode is removed and transferred via line 412 to replenish the supply of sulfide at 402. As shown in figure 8, sodium sulfide 414 (or another sulfide material) may be used as a starting sulfide material and to replenish any sulfide losses that may occur.

As a further benefit, the cathode reactions that are taking place to oxidise the iron sulfides also result in Fe(III) being released into solution. Therefore, the Fe(III) may also be returned to contact with further phosphate containing wastewater. This effectively recycles the Fe(III) through the process. This is shown that reference numeral 416 in figure 8. The iron sulfide oxidation reaction that takes place in the anode also reduces the solution pH. If the solution pH is reduced to below 2, the ferric ions remain in solution (avoiding Fe(OH)_3 formation). If necessary, some hydrochloric acid 418 may be added to achieve the required pH.

The process shown in figure 8 allows for recovery and recycle of both of the sulfide and the Fe(III) used in the process. This minimises the chemical supply requirements for the process.

In some embodiments, the first cathode solution from the second electrode compartment could be fed back in the first electrode compartment when it is used as cathode to achieve concentrated sulfide/polysulfide solution and vice versa. This process may be continued for each cycle to ultimately provide a very concentrated polysulfide/sulfide solution or alkaline solution. Thus, the process of the present

inventino may not only be a sulfide treatment process, it may also or alternatively be a sulfide concentration process.

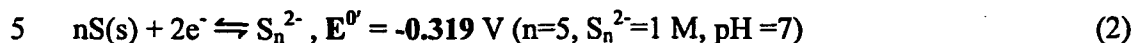
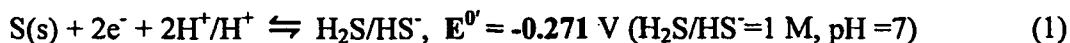
EXAMPLES

5

Sulfide is present in a wide range of industrial wastewaters such as tannery and paper mill wastewaters. It is toxic, corrosive and odorous and needs to be removed from wastewater before it is discharged into waterways. Sulfide discharges even to sewers are increasingly constrained due to the corrosive effects of sulfide in sewers, as well
10 as due to the odour and occupational health impacts in the sewers and downstream wastewater treatment plants. In a recent review on sewage sulfide removal, high cost was reported as one of the main disadvantages of the existing sulfide removal processes (Zhang et al., 2008). Recently, an electrochemical approach was proposed for wastewater sulfide removal, in which sulfide can be directly oxidized at an anode
15 (Rabaey et al., 2006). Elemental sulfur is the key oxidation product when carbon/graphite materials are used as the electrode material (Ateya et al., 2003). Potential advantages of electrochemical sulfide removal are cost effectiveness, selectivity, and controllability (Rajeshwar et al., 1994, Chen, 2004).

20 One of the main disadvantages of electrochemical sulfide removal is anode passivation by the precipitated elemental sulfur (Ateya et al., 2003, Reimers et al., 2006, Dutta et al., 2008). Extraction of sulfur by organic solvents and subsequent solvent evaporation or controlled sulfur precipitation in the bulk solution with alkali addition at elevated temperature were examined to prevent sulfur induced electrode
25 passivation or to regenerate electrodes (Shih and Lee, 1986, Mao et al., 1991). These strategies involve toxic organics and/or high energy input, and therefore are not considered as a sustainable approach. Recently, an electrochemical regeneration strategy was proposed that periodically switches between anode and cathode operation (Dutta et al., 2009a) . This approach allows for sulfide removal from
30 wastewater at the anode while at the cathode sulfur, previously precipitated on the electrode, is reduced to sulfide/polysulfide. As a result, the electrode is regenerated (see equation 1-3) and a concentrated sulfide/polysulfide solution can be obtained at the cathode with high coulombic efficiency. At high pH the coulombic efficiency can

even increase to above 100% as under those conditions the electrochemical removal is assisted by the chemical dissolution of sulfur by sulfide to polysulfides (equation 4).



Sulfide containing domestic or industrial wastewater will often contain a wide range of organic and inorganic compounds, trace elements and suspended particulate materials. All these may significantly influence the electrochemical sulfide removal process, particularly during long time operation. The organics may stimulate biofilm formation at the anode. Microorganisms in this biofilm can use electrodeposited sulfur as a preferred electron acceptor and release the sulfide irrespective of electrochemical conditions (Dutta et al., 2009b). This release can negatively affect the efficiency of the electrochemical sulfide removal process.

To our knowledge, no studies have yet examined electrochemical sulfide removal from real wastewater considering the possible bacterial interaction with sulfide oxidation products, the effect of sulfur precipitation and electrode regeneration, as well as the influence of other constituents such as suspended particulate materials on the oxidation rate. Therefore, this study aimed to demonstrate electrochemical sulfide removal from the effluent of an anaerobic treatment plant operated on paper mill wastewater. In addition, an operating approach to avoid biofilm formation was developed. Finally, a strategy was derived for the recovery of wastewater sulfide as concentrated sulfide/polysulfide solution from which solid elemental sulfur can be obtained.

MATERIALS AND METHODS

30

Wastewater Characteristics. The sulfide containing wastewater used in this study was collected at the exit of a high rate anaerobic treatment process. The plant receives

wastewater from the paper recycling plant and uses an Upflow Anaerobic Sludge Blanket (UASB) process to treat the wastewater before discharging the effluent into the sewer system. The typical characteristics of the effluent used in this study are shown in Table 1.

5

Electrochemical cell design and operation. The electrochemical cell was constructed according to Dutta et al. (2008), consisting of two identical rectangular chambers used as anode and cathode (volume 335 ml each) and was separated by a cation exchange membrane (Ultrex, CM17000, Membranes International Inc.).

10 Throughout this example, the two identical chambers of the cell are referred to as side 1 and side 2.

Two types of electrodes were used: carbon brushes and graphite granules. Carbon fibre (SGL Group) brushes were made with a twisted stainless steel core as described
15 by Logan et al. (2007). These brushes were used as electrodes for both chambers. The electrodes were connected with the external circuit via the stainless steel core. All experiments were conducted with brush electrodes unless stated otherwise. Electrodes made with graphite granules (El Carb 100, Graphite Sales Inc.) were only used to
20 examine sulfide removal rates at different loading rates and to compare the performance with carbon fibre brush electrodes. An Ag/AgCl (RE-5B, Bio-Analytical) electrode was used as the reference electrode (+197 mV vs. standard hydrogen electrode, SHE). The coulombic efficiency (CE) was calculated as the ratio between the measured amount of charge transferred in the process and the amount of charge transfer theoretically expected from the measured amount of sulfide removal
25 (based on the two electron sulfide oxidation to sulfur).

Table 1. Typical characteristics of the anaerobic treatment effluent wastewater of VISY paper mill wastewater treatment plant

	Parameters	Values
5	pH	7.3-7.6
	Conductivity (mS cm ⁻¹)	1.5-4.5
	COD (mg L ⁻¹)	1300-3000
	Volatile Fatty Acids (mg L ⁻¹)	
	acetic acid	250-680
10	Propionic acid	450-1100
	butyric acid	0-30
	iso-valeric acid	5-15
	valeric acid	0-20
	Sulfide-S (mg L ⁻¹)	35-55
15	TSS (mg L ⁻¹)	400-1200
	Ca ⁺ (mg L ⁻¹)	200-400
	Cl ⁻ (mg L ⁻¹)	220-280
	Na ⁺ (mg L ⁻¹)	900-1300
	K ⁺ (mg L ⁻¹)	50-70
20	Total N (mg L ⁻¹)	14-30
	Total P (mg L ⁻¹)	1-4

Both the anodic and cathodic solutions were recirculated with a peristaltic pump (Watson Marlow) at a flow rate of 12 L h⁻¹. A buffer flask of 1 litre was included in the cathodic recirculation line. The cathodic regeneration solution contained only 1 g L⁻¹ NaCl. Wastewater was pumped continuously into the anode chamber for all experiments using a peristaltic pump (Watson Marlow) with a flow rate of 8 L day⁻¹ unless otherwise mentioned. A balloon filled with nitrogen gas was connected to the top of the 25 litres wastewater drum to compensate for the liquid drawn from the drum while avoiding leakage of oxygen into the drum. The cell was operated potentiostatically with a controlled anode potential of +0.2 V vs. SHE using a potentiostat (VMP3, PAR). Current, cathode potential and cell voltage data were monitored for all experiments. Anode inlet and outlet samples were collected daily to

analyse dissolved sulfur species. First, the cell was operated for 2 days with synthetic wastewater containing only sulfide concentration of 50 mg-S L^{-1} (no organics) in 50 mM phosphate buffer and 1 g L^{-1} NaCl to compare the sulfide removal rate with real wastewater. Subsequently, the cell was operated on the wastewater obtained from an anaerobic treatment effluent described in Table 1.

Continuous wastewater experiments. All experiments with wastewater were divided into four different sets. The first sets of experiments were conducted to verify the probable impacts of the presence of different organic and inorganic compounds and suspended particulates on the sulfide removal rate. This experiment also investigated the cell performance in the presence of biofilm formation and sulfur deposition on the electrode surface. The cell was operated continuously until the sulfide removal stopped. After 10 days, the cell was run with synthetic wastewater (composition as mentioned above, no organics) for one day containing $50 \text{ mg of S L}^{-1}$ to examine possible effects of different constituents present in real wastewater on the sulfide removal. The cathode solution was changed and the organics inlet and outlet concentration were measured every three days. After the sulfide removal stopped, carbon fibres were collected from the anode chamber and prepared for microscopic analysis via Scanning Electron Microscope (SEM). Afterwards 500 ml sodium hypochlorite solution (17.5 g L^{-1} NaOCl, commercial laundry bleach) was recirculated through the anode chamber for about half an hour to inactivate a possibly formed biofilm. Then the cell was again operated for two more days with wastewater to compare the sulfide removal rate.

The second set of experiments was conducted to avoid biofilm formation during sulfide removal. This was done by periodic switching between anode and cathode (side 1 and side 2). For the first 18 days, the chamber was switched over every three days. Then a NaOCl solution (17.5 g L^{-1}) was recirculated for about half an hour through both chambers and the electrode was washed thoroughly. Subsequently the cell was operated for 21 days using periodic switching between anode and cathode in 24 hour intervals. Every cycle started with a new 500 ml cathode solution. Before switching over the chambers, all solutions were drained from the chambers, which were then washed 2 times with fresh water before refilling with the new solutions for

the start of the next cycle. Samples were collected after 18 ± 3 hours of starting each cycle.

The third set of experiments was conducted to obtain a concentrated sulfide/polysulfide solution, and operated by switching over the chambers every 24 hours. For this purpose, the same 500 ml cathode solution was used for five consecutive cycles (experiment repeated three times). To recover the removed sulfide as solid elemental sulfur, first a polysulfide rich solution was obtained. For this purpose, two 500 ml cathode solutions were used, one during the first 8 hours (primarily sulfur to sulfide/polysulfide reduction and chemical sulfur dissolution to polysulfide) and the other for the rest 16 hours (mainly hydrogen and alkaline production) of a particular 24 hour cycle. Similar to previous experiments, the same cathode solution was used for 5 consecutive cycles in both cases.

The fourth set of experiments was performed to evaluate the effects of loading rates (kg-S m^{-3} of total anode compartment (TAC) day^{-1}) on the sulfide removal rate. These experiments also examined the difference between carbon fibre brushes and graphite granules electrodes on the sulfide removal rate at different loading rates. Two identical reactors but with different electrodes were fed from the same wastewater feed tank at flow rates of 4, 8, 16, 24 and 32 L day^{-1} . The cell was operated for one day for each loading rate in both electrode sides by switching over every 24 hours.

Chemical analyses. Sulfide (H_2S , HS^- and S^{2-}), sulfite (SO_3^{2-}), sulfate (SO_4^{2-}) and thiosulfate ($\text{S}_2\text{O}_3^{2-}$) and concentrations were measured by ion chromatography (IC), using a Dionex 2010i system, according to Keller-Lehman et al. (2006). Samples collected from the reactors were immediately preserved in previously prepared Sulfide Antioxidant Buffer (SAOB) solution prior to ion chromatography analysis. SAOB solution was also used to dilute the samples where necessary. To measure total dissolved sulfur species including polysulfide concentrations, all sulfur species were oxidized to sulfate with H_2O_2 (after increasing the pH to around 12.5 with 0.4M NaOH) (Cloke, 1963). The difference between the sulfate after H_2O_2 oxidation and other species measured before H_2O_2 oxidation was regarded as polysulfides. Volatile fatty acid (VFA) concentrations were determined using a LC-10ADVP HPLC system

(Shimadzu). The VFA species analysed included acetic, propionic, butyric, isobutyric, valeric and isovaleric.

Electron microscopy and spectroscopy. The microscopic images of carbon fibres were collected using a Scanning Electron Microscope (SEM) (JEOL JSM 6400 & 6460 LA). The Secondary Electron (SE) detector provided the shape of the specimen whereas a Back Scattered Electron (BSE) detector produced images with compositional contrast. SEM images were taken to examine biofilm formation and deposition of any other constituents on the electrode surface. Before analysis, both fibre and sulfur samples were coated with platinum for 3 and 10 minutes respectively with a Sputter Coater. This was done to provide conductive coating of the SEM samples. The JEOL JSM 6460 was equipped with Energy Dispersion Spectrometry (EDS) which was used for detection of different elements.

15 RESULTS AND DISCUSSION

Continuous operation of the cell . At the anode potential of +0.2 V vs SHE, sulfide present in the wastewater was oxidized to sulfur in the anode, which deposited on the electrode according to equation (1). This was confirmed by measuring the inlet and outlet concentrations of different sulfur species. Only sulfide concentration was decreased while the concentration of other sulfur oxyanions did not change. The concentrations of sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}) were negligible ($<2\%$ of sulfide-S mg L^{-1}) and approximately 5% of sulfide-S was found as thiosulfate ($\text{S}_2\text{O}_3^{2-}$) both in the inlet and outlet which might be due to the oxidation of sulfide with oxygen during sample collection and preservation as reported earlier (Dutta et al., 2008). In the cathode, hydrogen evolution from water reduction was preferred. This process is associated with a high overpotential at non catalysed carbon fibre electrodes, causing a cell voltage of 1.1 to 1.5 V for currents ranging from 14 to 50 mA (0.83 to 2.97 A m^{-2} of membrane surface area). The obtained current from the anode can either be caused by sulfide oxidation or organics oxidation. No current was observed when the cell was operated with NaCl containing electrolyte. This confirms that the stainless steel core used in this experiment did not corrode at anode potential of +0.2V SHE.

Figure 9 shows a gradual decrease of the sulfide-S removal over time, decreasing from 85% to a negligible removal after about 15 days of continuous operation. During this period, the current increased from 14 to 50 mA. After 13 days, the outlet sulfide concentration was higher than the inlet concentration. Deactivation of the electrode due to the deposition of elemental sulfur or other wastewater constituents can cause a decrease of the sulfide removal rate (Dutta et al., 2008). To investigate this, the electrode surface coverage after 18 days of operation was evaluated by SEM.

The electron microscopy images (Fig. 10A & 10B) show the presence of bacteria and particulate materials in many locations. However, substantial areas of the carbon fibre remained bare. EDS analysis on the bare areas showed only a carbon peak, confirming that they are the uncovered carbon fibres (Fig. 10C & 10D). This implies that the decrease of sulfide removal was not caused by the deposition of sulfur or other chemical constituents/particulate materials on the electrode fibres. Moreover, passivation of the electrode would have caused decreasing currents, but when the sulfide removal stopped, the highest currents of the experiment were observed. Analyses elucidated that at this time 160 ± 25 mg of COD (calculated from VFA concentrations) was consumed, while in the initial phase no significant change in COD concentrations was observed. These results corroborate the observed formation of a biofilm on the electrode surface. The bacteria likely reduced elemental sulfur back to sulfide after it formed electrochemically and they were using organics as electron donor (Dutta et al., 2009b). This was also supported by the occurrence of a negative sulfide removal rate from day 13, which was likely the result of sulfide production from sulfur previously deposited on the electrode. At that point the sulfide generation rate by bacteria might be higher than electrochemical sulfide oxidation rate. This finding was further confirmed when the sulfide removal rate was restored to about 82% of the initial value when the biofilm was killed with NaOCl after 18 days of operation.

A higher sulfide removal rate was observed when synthetic wastewater (no organics) replaced the effluent of an anaerobic treatment process after 10 days. This suggests that biological sulfur reduction did not occur in the absence of organics. It is important to note that sulfide was removed from synthetic wastewater at almost the same rate as those observed for real wastewater on Day 1, and for synthetic

wastewater at the start of the experiment prior to any wastewater addition. This indicates that particulate materials and soluble constituents as such do not directly affect the electrochemical sulfide removal.

- 5 The anaerobic process effluent used here contains high levels of COD ($2100 \pm 800 \text{ mg L}^{-1}$) relative to only $44 \pm 7 \text{ mg}$ of sulfide-S L^{-1} . The COD allows rapid biofilm development on the electrode surface, basically converting the cell into a microbial electrolysis cell for organics oxidation (Logan, 2009). The high COD/sulfur ratio (i.e. the abundance of electron donor with respect to electron acceptor, elemental sulfur)
10 could be the reason for the net zero or even temporarily negative sulfide removal rate.

Bacteria can also directly use the anode as electron acceptor, in parallel to using the electrodeposited sulfur. The current obtained in the first 1-3 days could be considered as the maximum current obtainable from sulfide oxidation to elemental sulfur for the
15 used reactor, at the used loading rate. Higher currents than those obtained in the first 1-3 days indicate organics oxidation using the anode as electron acceptor which eventually confirms biofilm formation on the anode surface. In this case, bacteria in parallel could also use electrodeposited elemental sulfur as electron acceptor. Therefore, to ensure efficient sulfide removal, biofilm formation must be avoided or
20 regularly removed. We hypothesize that this can be achieved by periodic switching the polarity of the anode to cathodic mode. During cathodic reduction, the pH of the cathode electrolyte increases to levels toxic to most micro-organisms. Moreover, such periodic switching will be a very efficient way for the electrochemical regeneration of the sulfur loaded electrodes (Dutta et al., 2009a).

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Regular switching between anode and cathode.

In a second set of experiments, the anode and cathode polarity was reversed every 24 hours. During anodic oxidation, sulfide converted to sulfur which was deposited on
30 the electrode; upon reversing the polarity of the electrode, the sulfur is again reduced to sulfide or polysulfide. Moreover, at high pH the released sulfide reacts with sulfur to form additional polysulfide (see equations 1 to 3 and 5). Figure 11 shows that over a period of 21 days the sulfide removal rate ($81 \pm 4\%$) remained almost stable when operated at a flow rate of 8 L day^{-1} . The wastewater sulfide decreased from $44 \pm 7 \text{ mg-}$

S L⁻¹ to 8±2 mg-S L⁻¹ at a removal rate of 0.845±0.133 kg-S m⁻³ TAC d⁻¹. The required cell voltage during this operation was between 0.52 and 1.3 V. This value varied as the cathodic reaction shifted from sulfur/polysulfide reduction to hydrogen evolution. When all the sulfur/polysulfide was reduced to sulfide, the cathode potential suddenly dropped to a lower value as also observed and reported earlier (Dutta et al., 2009a). At the same time, the yellow color of the solution due to the presence of polysulfides had completely disappeared.

The obtained current was in the range of 14 to 25 mA, corresponding to coulombic efficiencies (CE) of 75% to 120% (considering two-electron sulfide oxidation to sulfur). The CE values for continuous sulfide oxidation from synthetic wastewater were less than 100% (i.e. 88±5%) due to autooxidation of sulfide to other dissolved sulfur species such as thiosulfate. In addition, bacteria and various chemical constituents present in real wastewater might also slightly contribute to such electron losses. CE values higher than 100% were observed during several cycles, notably in the last 5-6 hours of a 24 hour cycle (data not shown). This could be due to the initiation of biofilm development on the electrode surface and eventually for organics oxidation. Higher currents of up to 37 mA were noted at longer switching period of 72 h intervals which further supports organics oxidation. However, upon operating the cell at 72 h switching intervals over 18 days, the sulfide removal rate decreased from its initial value of 81±4% to around 57±3% (results not shown), again indicating biological sulfur reduction.

The variation of current (14 to 25 mA) as described above resulted in a variation of the pH in the cathode solution. The pH of the cathode solution increased to 9.5-11.3 in individual 24 hours cycles. In electrochemical systems that are operated on wastewater, cation exchange membranes predominantly transport cations such as Na⁺, K⁺, Ca²⁺ etc. as they are more abundant in wastewater compared to protons (Rozendal et al., 2006). Therefore, the OH⁻ generated at the cathode from sulfur reduction or hydrogen evolution cause an increased pH due to the lack of balancing protons from the anode. Such rapidly changing, high pH levels very likely inhibit or kill microorganisms that are attached to the electrode, therefore limiting the risk of sulfur loss due to biofilm formation. In a recent study, Gutierrez et al. (2009) also reported a 50% activity reduction of sulfate reducing bacteria due to the long term pH elevation

from 7.6 to 9 in a sewer system. However, a key challenge for practical operation will be to ensure sufficient current densities to reach desirable pH levels, as well as using a non-buffered cathode electrolyte. Overall, periodic switching serves a double purpose: i) avoiding biofilm formation or inhibiting bacterial activities and ii) reducing electrodeposited sulfur to sulfide/polysulfides and thus regenerating the electrode, which will be important for the ongoing operation to remove sulfide from real wastewater streams.

Recovery of wastewater sulfide.

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Instead of using a new cathode solution in every cycle, the same cathode solution was used for several cycles in an additional series of experiments. The repetitive use of the same cathode solution for 5 consecutive cycles allowed to reach higher pH values as well as more concentrated sulfide/polysulfide solutions; i.e. the pH increased to 12.3 and about 890 ± 50 mg of different sulfur species (of which $74 \pm 5\%$ of sulfide-S) were measured, corresponding to $75 \pm 4\%$ recovery of the removed sulfide. Besides sulfide, thiosulfate and sulfate were found in the recovered solution, representing about 26% of dissolved sulfur species. These could be formed through sulfide/polysulfide oxidation, as the solution was exposed to air during manual periodic switching and washing the chambers. The reasons for the recovery loss of around 25% of the sulfide removed are difficult to determine. Inefficiencies can be caused by some (concentrated) solution remaining in the reactor during polarity switching, as well as some variability of the influent over a batch cycle.

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Higher levels of sulfide are known to be toxic for many anaerobic bacteria (Lens et al., 1998). Therefore, repetitive usage of the same cathode solution for several cycles might provide an additional advantage of inhibiting microbial processes due to a combination of high sulfide concentrations and higher pH. However, the concentrated sulfide solution obtained from the cathodic process needs further treatment to obtain solid elemental sulfur or sulfate that be used for further applications. The further treatment could be done by chemical or biological oxidation preferably with oxygen. The oxidation of the (poly)sulfide to solid elemental sulfur is attractive as it generates a valuable product that can be easily harvested. Alternatively, the alkaline sulfide solution could be used for H_2S absorption in an anaerobic treatment off-gas

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desulfurisation unit of a full scale wastewater treatment process as illustrated by Janssen et al. (2009). In that particular case, liquid phase sulfide removal by the proposed process could provide additional advantages of sulfide recovery and production of alkaline solutions needed for a biogas desulfurisation unit. However, the alkaline concentrated sulfide solution could also be used to produce hydrogen and solid sulfur in a photocatalytic process using visible light or sunlight (Jang et al., 2006). The photocatalyst CdS is well known to produce hydrogen from water under visible light, but it suffers from photocorrosion without sacrificial agent. Generally alkaline sulfide solution are used as sacrificial agent to overcome this (Kudo and Miseki, 2009).

Polysulfide solutions are also promising electrolytes for electrochemical storage of energy and photoelectrochemical solar cells (Kamyshny et al., 2004). In addition, polysulfides may also improve the yield and quality of paper in the pulp and paper industry, an industry that generally produces sulfide-rich wastewaters (Chen and Miller, 2004). As intermediary towards sulfur recovery, polysulfide is preferred over sulfide. Concentrated polysulfide solutions can be converted to solid harvestable elemental sulfur by an easy step of either adjusting the pH to slightly acidic or near neutral or lightly aerating the solution. The abiotic oxidation kinetics of polysulfides is very fast relative to sulfide oxidation kinetics (Steudel, 2000, Van Den Bosch et al., 2008). Moreover, less electrons are needed to generate polysulfide.

From the repeatedly used cathode solution, approximately 400 mg of polysulfide-S was recovered (8 hours in each cycle over 5 cycles). When the pH of the polysulfide solution was adjusted to 5, solid elemental sulfur precipitated out immediately. Elemental sulfur was then collected, dried and analysed by EDS to examine its purity. The EDS analysis showed a dominant sulfur peak besides the small platinum peak caused by sputter coating (Figure 12). Thus, the EDS analysis demonstrated that pure elemental sulfur could be recovered from real wastewater. To maximize sulfur recovery by polysulfide formation, the process needs to be optimized towards polysulfide formation, which implies that the cathode solution needs to be removed before further reduction of polysulfide occurs.

Influence of operational parameters . The results reported and discussed above were obtained with a fixed feed flow rate of 8 L d^{-1} , which corresponds to a sulfide loading rate of $1.05 \pm 0.18 \text{ kg-S m}^{-3}$ of TAC d^{-1} . When the reactor was operated at different loading rates by varying the feed flow rates, different effluent sulfide-S concentrations were observed (Figure 13A). Graphite granules showed better performance in comparison to carbon fibre brush electrodes (Figure 13B). Higher loading rates provide higher currents from the anodic process (Figure 13B), allowing faster cathode regeneration and higher pH values. The downside of these increased loading rates was the elevated effluent sulfide-S concentrations (Figure 13A). Therefore, an appropriate loading rate needs to be selected considering the benefits of operation at higher loading rates and the discharge requirements for the effluent. Other critical factors involve the reactor size, hydrodynamic fluid flow patterns in the reactor, proper electrode materials, the input voltage etc. Larger scale operation will be necessary to accurately establish the life time and the economic cost/benefit ratio of the electrochemical sulfide removal/recovery relative to other methods.

Electrochemical sulfide removal from the effluent of an anaerobic treatment process of a paper mill wastewater treatment plant was evaluated in this example. Sulfide could be effectively removed by electrochemical process from real wastewater, although biofilm formation needs to be avoided. This was achieved by periodic anode and cathode switching as the pH of the cathode solution increased to inhibitory levels. The switching also allowed recovery of the sulfide as a concentrated, alkaline sulfide/polysulfide solution, from which pure solid elemental sulfur could be obtained.

Those skilled in the art will appreciate that the present invention may be susceptible to variations and modifications other than those specifically described. It will be understood that the present invention encompasses all such variations and modifications that fall within its spirit and scope.

Throughout this specification, the term "comprising" and its grammatical equivalents shall be taken to have an inclusive meaning unless the context of use indicates otherwise.

The applicant does not concede that the prior art discussed in the specification forms part of the common general knowledge in Australia or elsewhere.

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CLAIMS

1. A method for treating a sulfide containing solution comprising:
 - 5 a) providing an electrochemical system comprising a first electrode compartment having a first electrode and a second electrode compartment having a second electrode;
 - b) supplying the first electrode compartment with the sulfide containing solution and
10 operating the first electrode as an anode to oxidise sulfide to form elemental sulfur or other sulfur forms more oxidized than sulfide;
 - c) subsequently operating the first electrode compartment as a cathode and operating the second electrode compartment as an anode such that elemental sulfur or other
15 sulfur forms more oxidised than sulfide in the first electrode compartment is reduced to sulfide or polysulfide (or both) and feeding the sulfide containing solution to the second electrode compartment to oxidise sulfide to form elemental sulfur or other sulfur forms more oxidized than sulfide;
 - 20 d) subsequently operating the second electrode compartment as a cathode and operating the first electrode compartment as an anode such that sulfur or other sulfur forms more oxidised than sulfide in the second electrode compartment is reduced to sulfide or polysulfide (or both) and feeding the sulfide containing solution to the first
25 electrode compartment to oxidise sulfide to form sulfur or other sulfur forms more oxidised than sulfide;

wherein a cathode solution containing sulfide or polysulfide of enhanced concentration when compared to the solution fed to the anode is obtained.
- 30 2. A method as claimed in claim 1 further comprising sequentially repeating steps (c) and (d).
3. A method as claimed in claim 1 or claim 2 wherein a relatively small volume of solution is supplied to the cathode, when compared to the volume of solution

supplied to the anode, in order to form a cathode solution containing sulfide or polysulfide of enhanced concentration when compared to the solution fed to the anode.

- 5 4. A method as claimed in any one of the preceding claims wherein a first cathode solution from the second electrode compartment is fed back into the first electrode compartment when the first electrode compartment is used as cathode to achieve concentrated sulfide/polysulfide solution and vice versa.
- 10 5. A method as claimed in any one of the preceding claims wherein the electrode that is operated as a cathode is initially provided with a first cathode solution in which sulfide or polysulfide (or both) is formed, and subsequently provided with a second cathode solution and the cathode is operated such that pH of the second cathode solution increases.
- 15 6. A method as claimed in claim 5 wherein the second cathode solution is provided to the cathode at or near a time when sulfur or other sulfur forms more oxidised than sulfide in or on the cathode has been fully reacted to form sulfide or polysulfide (or both).
- 20 7. A method as claimed in claim 6 wherein product streams from the cathode comprise a first solution containing sulfide or polysulfide (with the sulfide being of enhanced concentration relative to the concentration of the sulfide fed to the anode compartment) and a second cathode solution that has an alkaline pH.
- 25 8. A method as claimed in claim 7 wherein the second cathode solution has a pH of greater than 10, more preferably greater than 11, even more preferably greater than 12, most preferably greater than 13.
- 30 9. A method as claimed in claim 7 or claim 8 wherein the pH of the first cathode solution is greater than about 9.
10. A method as claimed in any one of the preceding claims further comprising providing an electrochemical system that includes a third electrode compartment

containing a third electrode, the third electrode being operated as a cathode when reduction of sulfur to sulfide or polysulfide (or both) in the first electrode compartment or second electrode compartment is nearly or essentially complete.

- 5 11. A method as claimed in claim 10 wherein the third electrode compartment is always operate as a cathode.
- 10 12. A method as claimed in any one of claims 1 to 10 comprising providing an electrochemical system that includes a third electrode compartment containing a third electrode, each of the first electrode, second electrode and third electrode being sequentially operated as the anode such that sulfide in the sulfide containing solution fed to the anode is oxidised to form sulfur or other sulfur forms more oxidized than sulfide on the anode to thereby sequentially load the first electrode, second electrode and third electrode with sulfur or other sulfur forms more oxidized than sulfide, subsequently operating the electrode loaded with sulfur or other sulfur forms more oxidized than sulfide as a cathode to form a solution containing sulfide or polysulfide (or both) whilst at the same time operating one of the other electrodes as the anode to thereby load the anode with sulfur or other sulfur forms more oxidized than sulfide, wherein when sulfur or other sulfur forms more oxidized than sulfide in the cathode is nearly or essentially exhausted, the remaining electrode is operated as a cathode to thereby generate an alkaline containing solution.
- 15 20 25 30 13. A method as claimed in any one of the preceding claims wherein reduction of sulfur or other sulfur forms more oxidized than sulfide at the cathode forms a polysulfide containing solution and the polysulfide containing solution is recovered for subsequent use, or the polysulfide containing solution is treated to form a sulfide containing solution of enhanced sulfide concentration when compared to the sulfide containing solution fed to the anode or the polysulfide solution is treated to form elemental sulfur.
14. A method as claimed in any one of the preceding claims wherein the sulfide containing solution that is fed to the anode in the present invention comprises a sulfide containing wastewater.

15. A method as claimed in any one of claims 1 to 12 or 14 wherein a sulfide containing solution is formed in order to recover and recycle sulfide to another process that requires sulfide as a feed input.
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16. A method as claimed in any one of the preceding claims wherein the liquid stream provided to the anode has a pH higher than 7 such that sulfur precipitating on the anode reacts with solution sulfide to form polysulfide.
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17. A method as claimed in claim 16 wherein the electrochemical system is operated sufficiently long to oxidize all sulfide and subsequently polysulfide to elemental sulfur at the anode.
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18. A method as claimed in any one of the preceding claims wherein the electrode compartments are separated from each other by an ion permeable membrane.
19. A method as claimed in claim 18 wherein the ion permeable membrane allows the passage of cations therethrough or the ion permeable membrane comprises a non-ion selective separator.
- 20
20. A method as claimed in any one of the preceding claims wherein the cathode solution of the electrochemical system is used to capture sulfide from a gaseous stream.
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21. A method as claimed in claim 20 wherein consumption of protons in the cathode leads to increasing pH which allows capture of sulfide in the cathode solution, while simultaneously sulfur or other sulfur forms more oxidized than sulfide is reduced to sulfide at the cathode.
- 30
22. A method as claimed in claim 20 or claim 21 wherein a bioelectrochemical or further electrochemical system is used to capture sulfide from a gaseous stream at the cathode, after which the effluent of this cathode is sent to the electrochemical system for recovery of the sulfide in a separate stream.

23. A method as claimed in claim 22 wherein the effluent of the electrochemical system, now low in sulfide, is returned to the bioelectrochemical or further electrochemical system for further sulfide recovery.
- 5 24. A method as claimed in any one of the preceding claims wherein the cathode of a bioelectrochemical or another electrochemical system is used to capture both CO₂ and sulfide from a gaseous stream and the effluent of this cathode is sent to the electrochemical system for recovery of the sulfide while the CO₂ remains in the fluid or is stripped into a separate, gaseous phase.
- 10 25. An electrochemical system comprising a first electrode compartment having a first electrode, a second electrode compartment having a second electrode and a third electrode compartment having a third electrode, the first electrode compartment being provided with an anode solution inlet for supplying an anode solution thereto and cathode solution inlet for supplying a first cathode solution thereto, the
- 15 second electrode compartment being provided with anode solution inlet for supplying an anode solution thereto and cathode solution inlet for supplying a first cathode solution thereto, the third electrode compartment being provided with a second cathode solution inlet for supplying a second cathode solution thereto.
- 20 26. A system as claimed in claim 25 wherein the first electrode and the second electrode are arranged such that the first electrode sequentially operates as an anode and a cathode and the second electrode sequentially operates as a cathode and an anode, with the third electrode operating as a cathode.
- 25 27. An electrochemical system comprising a first electrode compartment having a first electrode, a second electrode compartment having a second electrode and a third electrode compartment having a third electrode, the first electrode compartment being provided with an anode solution inlet for supplying an anode solution thereto and at least one cathode solution inlet for supplying a first cathode solution thereto and for supplying a second cathode solution thereto, the second electrode compartment being provided with an anode solution inlet for supplying an anode solution thereto and at least one cathode solution inlet for supplying a first cathode solution thereto and for supplying a second cathode solution thereto and the third
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electrode compartment being provided with anode solution inlet for supplying an anode solution thereto and at least one cathode solution inlet for supplying a first cathode solution thereto and for supplying a second cathode solution thereto.

- 5 28. A system as claimed in claim 27 wherein the first electrode, the second electrode and the third electrode are electrically connected such that one of the electrodes is operated as an anode, another of the electrodes is operated as a first cathode to reduce sulfur or other sulfur forms more oxidized than sulfide on that cathode and the other of the electrodes is operated as a second cathode to form an alkaline
10 solution when sulfur or other sulfur forms more oxidized than sulfide on the other cathode is exhausted, and the first electrode, second electrode and third electrode each sequentially operate as the anode, the first cathode and the second cathode.
- 15 29. A system as claimed in any one of claims 25 to 28 wherein the electrochemical system is provided with electrical switching in order to allow the electrodes to be switched between anodic and cathodic operation and the electrochemical system is provided with appropriate valving on all influent lines and effluent lines to control the flow of liquid to and from the respective electrode compartments and to ensure that the desired liquid is provided at the desired time to the desired electrode
20 compartment.
- 25 30. A method for treating a metal phosphate containing material comprising the steps of adding sulfide to the metal phosphate containing material to form metal sulfide precipitates whilst releasing phosphate into solution, separating a phosphate containing solution from the metal sulfide precipitates, feeding the metal sulfide precipitates to an electrochemical system comprising a first electrode compartment having a first electrode and a second electrode compartment having a second electrode, supplying the first electrode compartment with metal sulfide and operating the first electrode as an anode to oxidise metal sulfide to form sulfur
30 or another form of sulfur that is more oxidised than sulfide and metal ions, subsequently operating the first electrode compartment as a cathode and operating the second electrode compartment as an anode such that sulfur or another form of sulfur that is more oxidised than sulfide in the first electrode compartment is reduced to sulfide or polysulfide (or both) and supplying the second electrode

compartment with the metal sulfide to oxidise sulfide to form sulfur, recovering a sulfide containing solution from the electrode compartment that is operating as a cathode and returning the sulfide containing solution to be mixed with the metal phosphate containing material.

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31. A method as claimed in claims 30 wherein the metal sulfide comprises a sulfide containing iron, arsenic, aluminium, cobalt, copper, nickel, silver, cadmium, barium, calcium, manganese, mercury, lead, zinc, magnesium or mixtures of two or more thereof.

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32. A method as claimed in claim 30 or claim 31 wherein the metal phosphate material comprises an iron phosphate sludge and the method comprises treating an iron phosphate containing sludge comprising the steps of adding sulfide to the iron phosphate containing sludge to form iron sulfide precipitates whilst releasing phosphate into solution, separating a phosphate containing solution from the iron sulfide precipitates, feeding an aqueous mixture containing the iron sulfide precipitates to an electrochemical system comprising a first electrode compartment having a first electrode and a second electrode compartment having a second electrode, supplying the first electrode compartment with the iron sulfide containing aqueous mixture and operating the first electrode as an anode to oxidise iron sulfide to form sulfur or another form of sulfur that is more oxidised than sulfide and ferric (Fe(III)) or ferrous (Fe(II)) ions (or both), subsequently operating the first electrode compartment as a cathode and operating the second electrode compartment as an anode such that sulfur or another form of sulfur that is more oxidised than sulfide in the first electrode compartment is reduced to sulfide or polysulfide (or both) and supplying the second electrode compartment with the iron sulfide to oxidise sulfide to form sulfur or another form of sulfur that is more oxidised than sulfide, recovering a sulfide containing solution from the electrode compartment that is operating as a cathode and returning the sulfide containing solution to be mixed with the iron phosphate containing sludge.

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33. A method as claimed in claim 32 wherein the iron phosphate containing sludge is formed by mixing a solution containing ferric or ferrous ions (or both) with a solution containing dissolved phosphate and a solution containing ferric or ferrous

ions (or both) is recovered from the electrode compartment operating as the anode and the solution containing ferric or ferrous ions (or both) is returned to be mixed with the solution containing dissolved phosphate to form further iron phosphate containing sludge.

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34. A method as claimed in claim 32 or claim 33 wherein the method comprises operating one of the electrode compartments as an anode to form elemental sulfur on the anode whilst, at the same time, operating the other electrode compartment as a cathode so that elemental sulfur deposited on that electrode is reduced to sulfide or polysulfide (with the polysulfide subsequently being transformed into sulfide), and once the anode is loaded with elemental sulfur, the anode and cathode are switched so that the electrode loaded with elemental sulfur becomes the cathode and the elemental sulfur on the cathode is reduced to polysulfide and sulfide.

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35. A method as claimed in claim 34 wherein the cathode compartment is operated for part of a cathode cycle to recover a sulfide containing solution and for a later part of the cathode cycle to recover an alkaline solution when the elemental sulfur on the cathode has been exhausted.

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36. A method as claimed in claim 35 further comprising providing an electrochemical system that includes a third electrode compartment containing a third electrode, the third electrode being operated as a cathode when reduction of sulfur to sulfide or polysulfide (or both) in the first electrode compartment or second electrode compartment is nearly or essentially complete.

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37. A method as claimed in claim 36 wherein the third electrode compartment is always operate as a cathode.

38. A method as claimed in claim 35 comprising providing an electrochemical system that includes a third electrode compartment containing a third electrode, each of the first electrode, second electrode and third electrode being sequentially operated as the anode such that sulfide in the sulfide containing solution fed to the anode is oxidised to form sulfur or other sulfur forms more oxidized than sulfide

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on the anode to thereby sequentially load the first electrode, second electrode and third electrode with sulfur or other sulfur forms more oxidized than sulfide, subsequently operating the electrode loaded with sulfur or other sulfur forms more oxidized than sulfide as a cathode to form a solution containing sulfide or polysulfide (or both) whilst at the same time operating one of the other electrodes as the anode to thereby load the anode with sulfur or other sulfur forms more oxidized than sulfide, wherein when sulfur or other sulfur forms more oxidized than sulfide in the cathode is nearly or essentially exhausted, the remaining electrode is operated as a cathode to thereby generate an alkaline containing solution.

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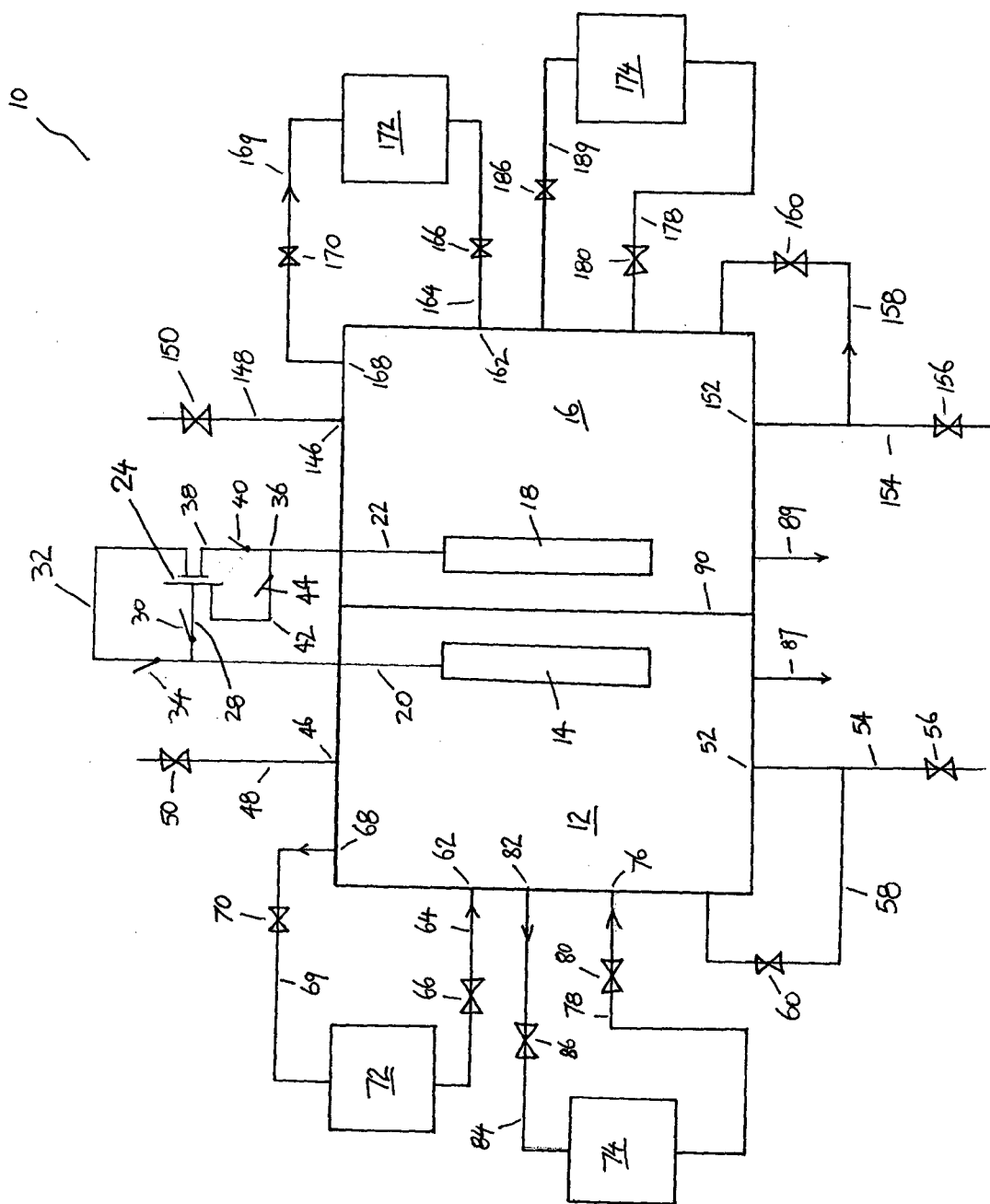


FIGURE 1

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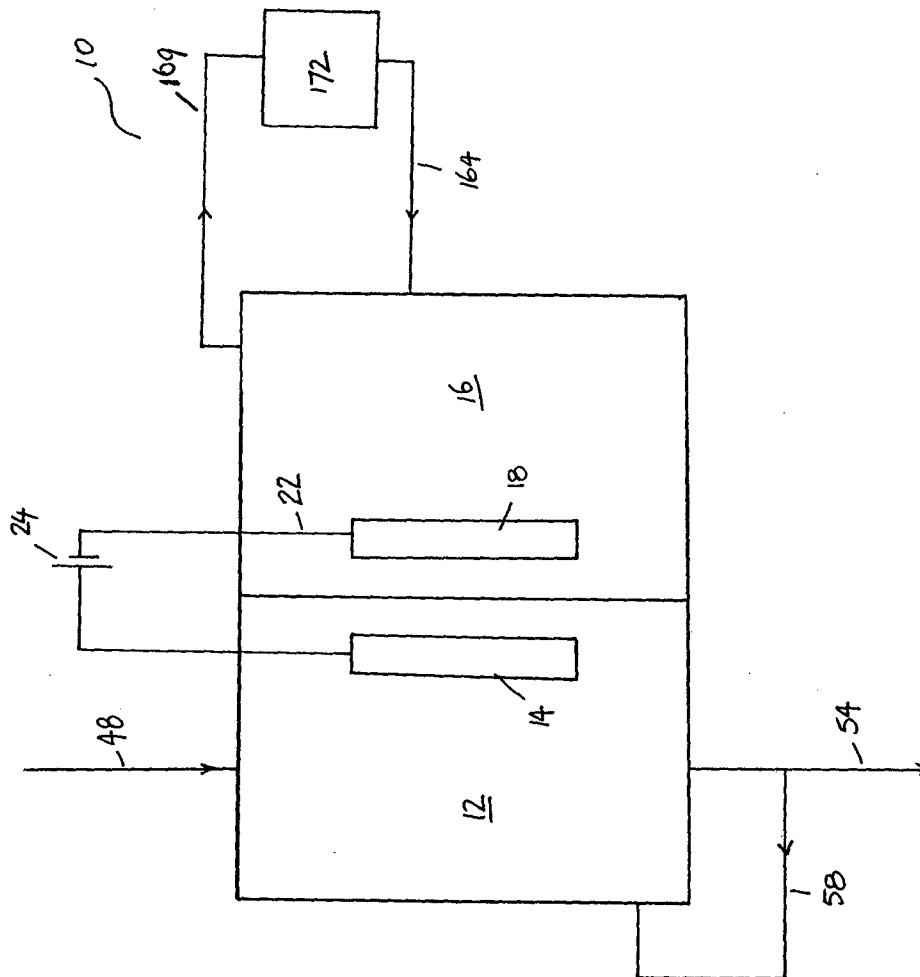


FIGURE 2

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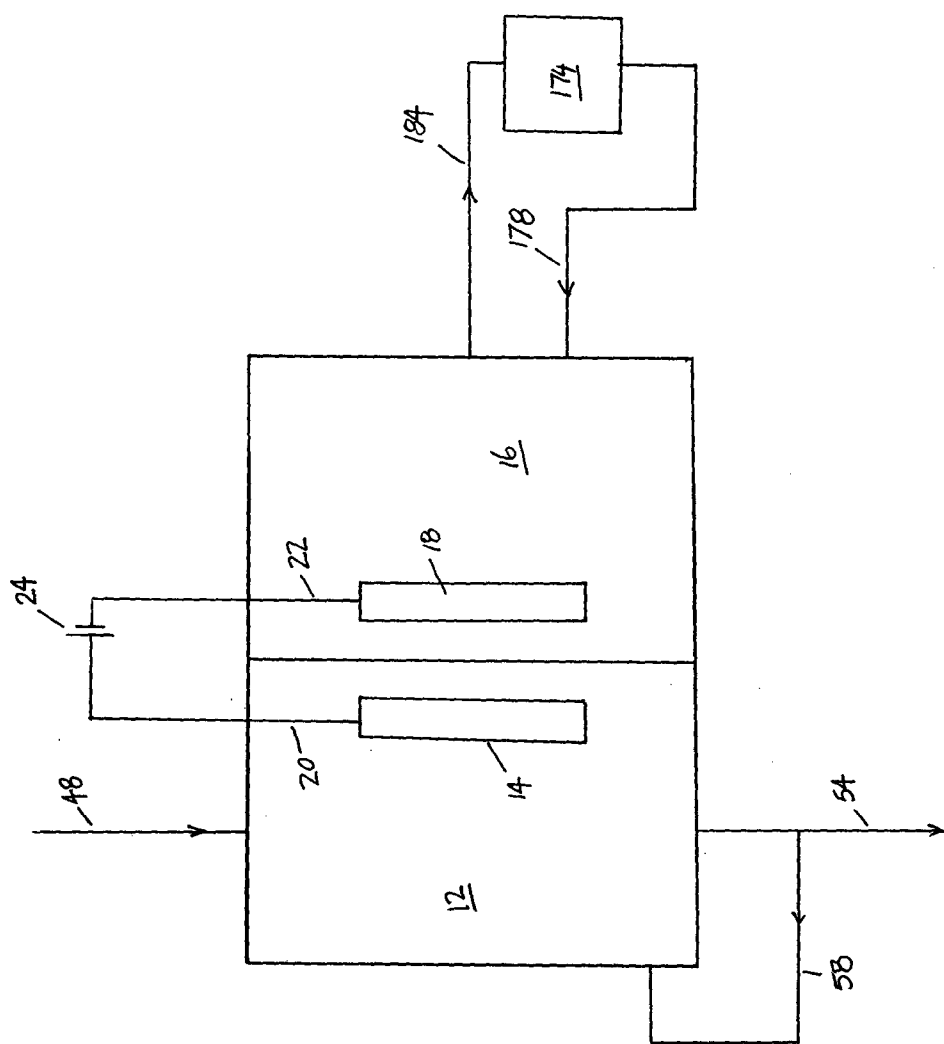


FIGURE 3

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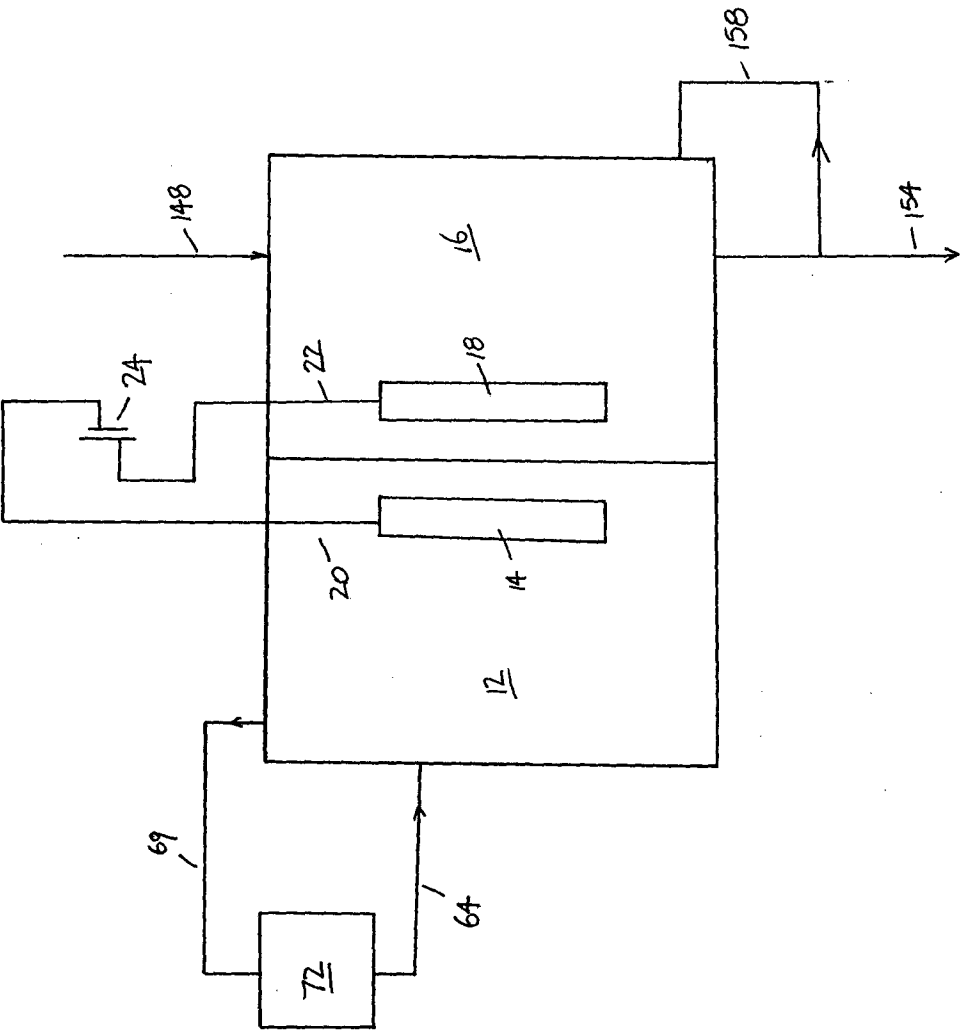


FIGURE 4

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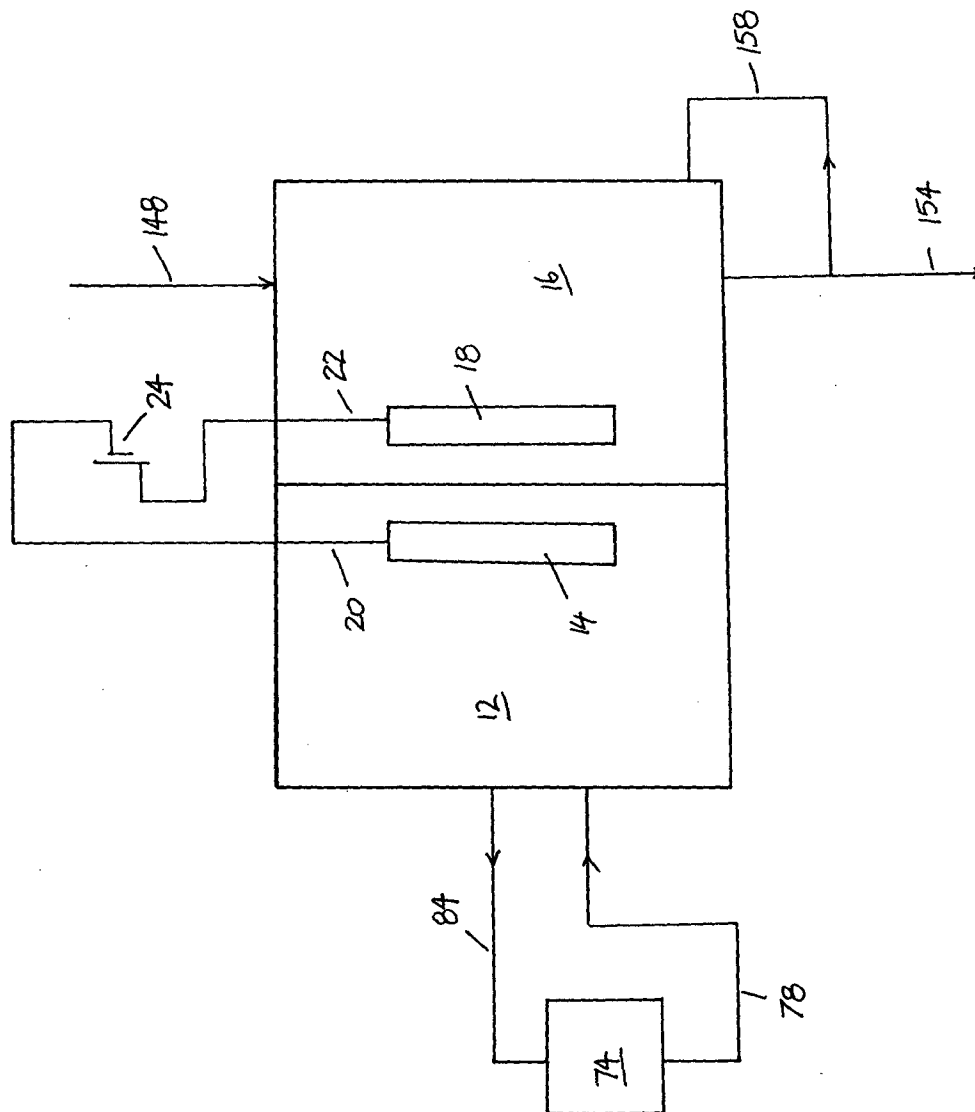


FIGURE 5

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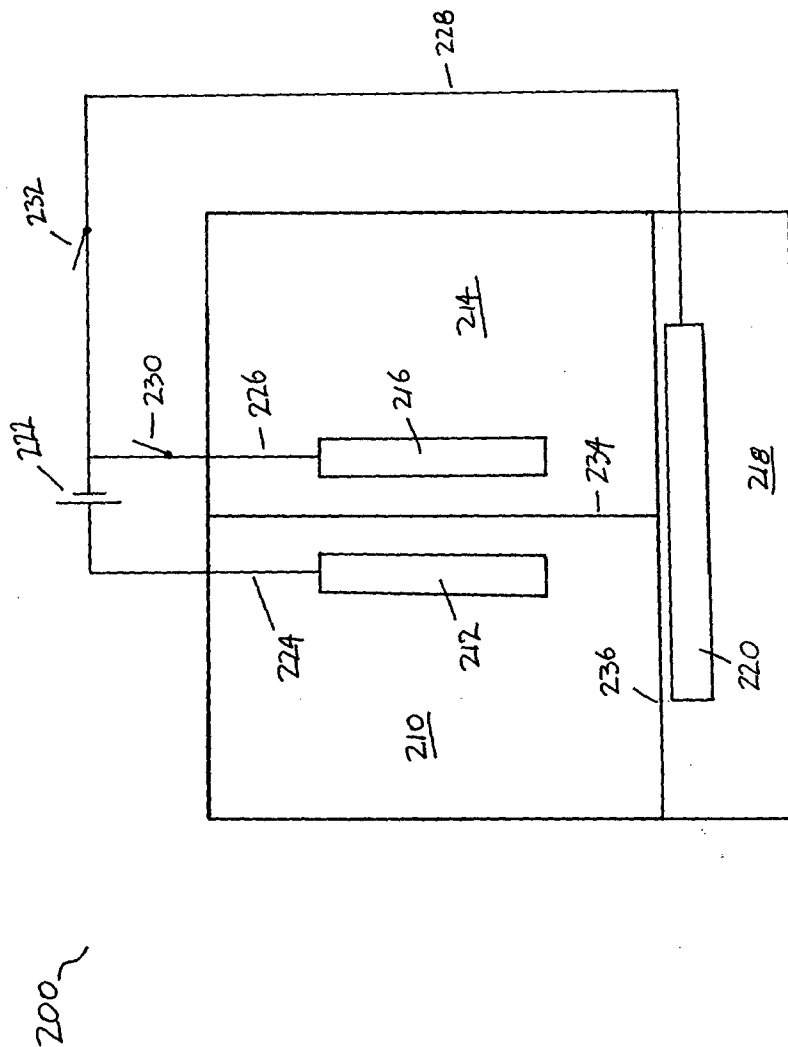


FIGURE 6

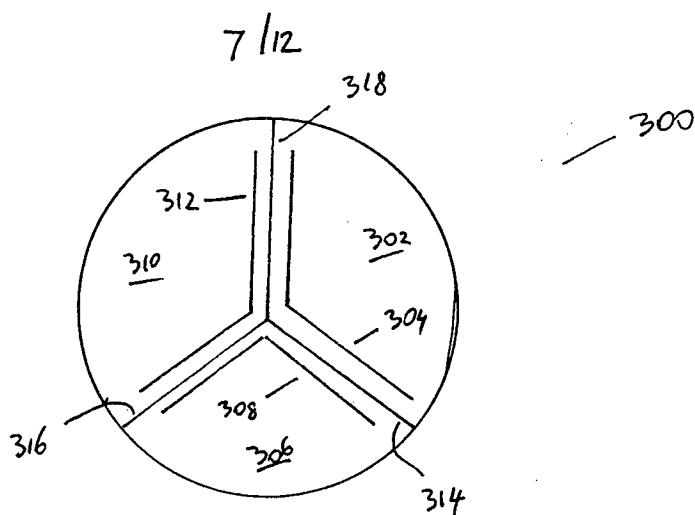


FIGURE 7

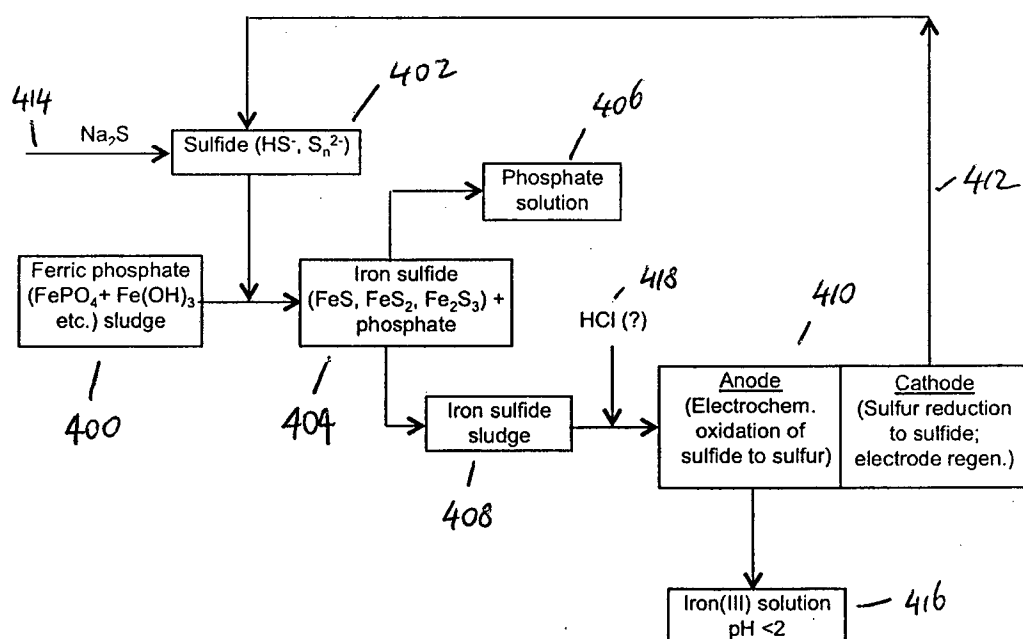


FIGURE 8

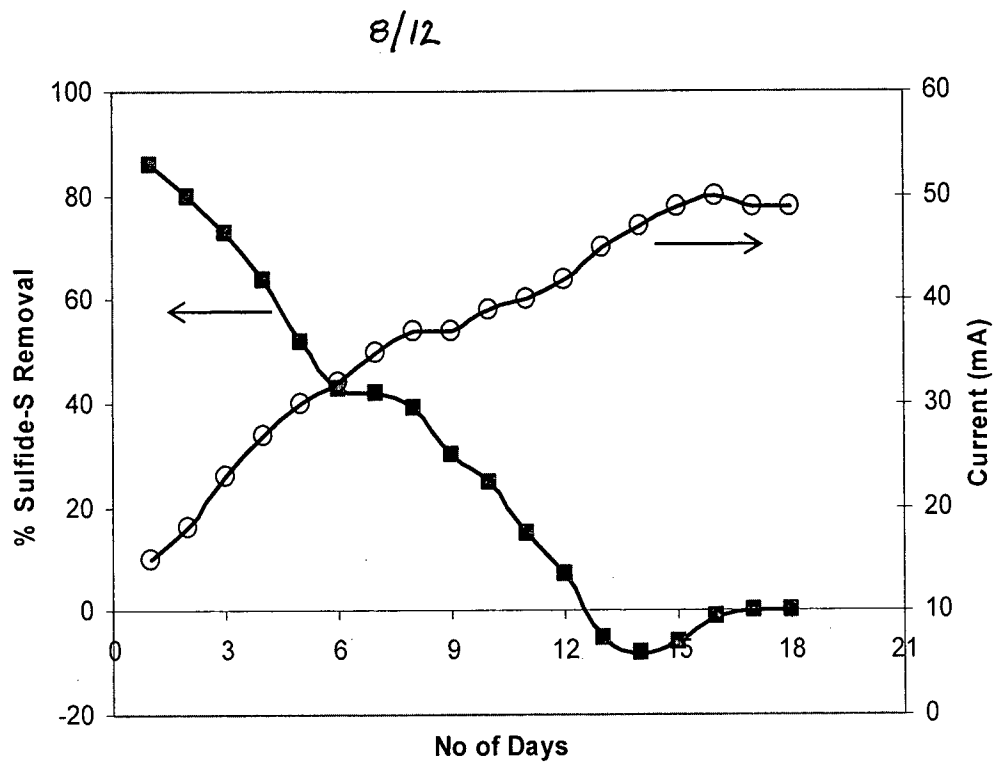


Figure 9.

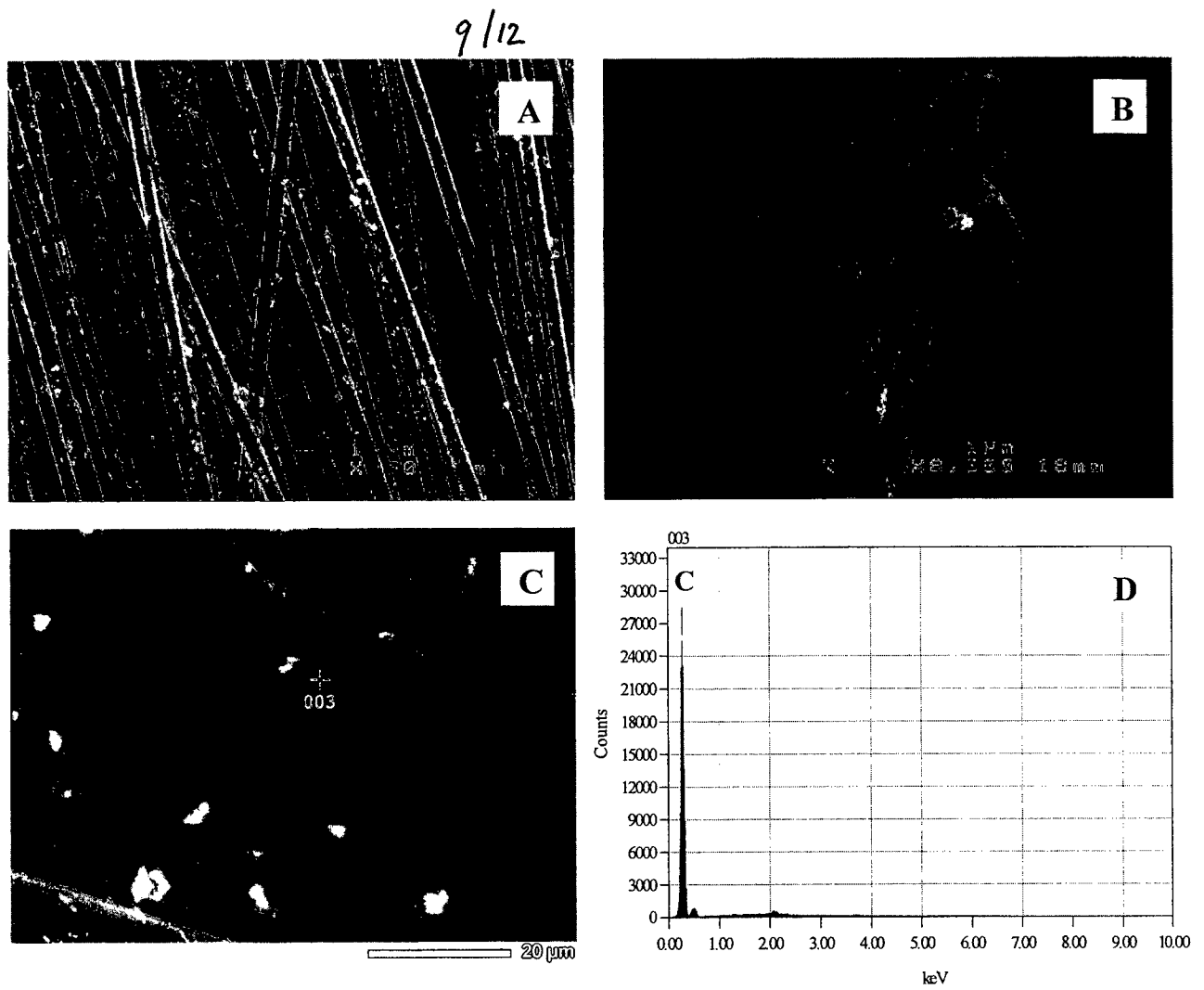


Figure 10.

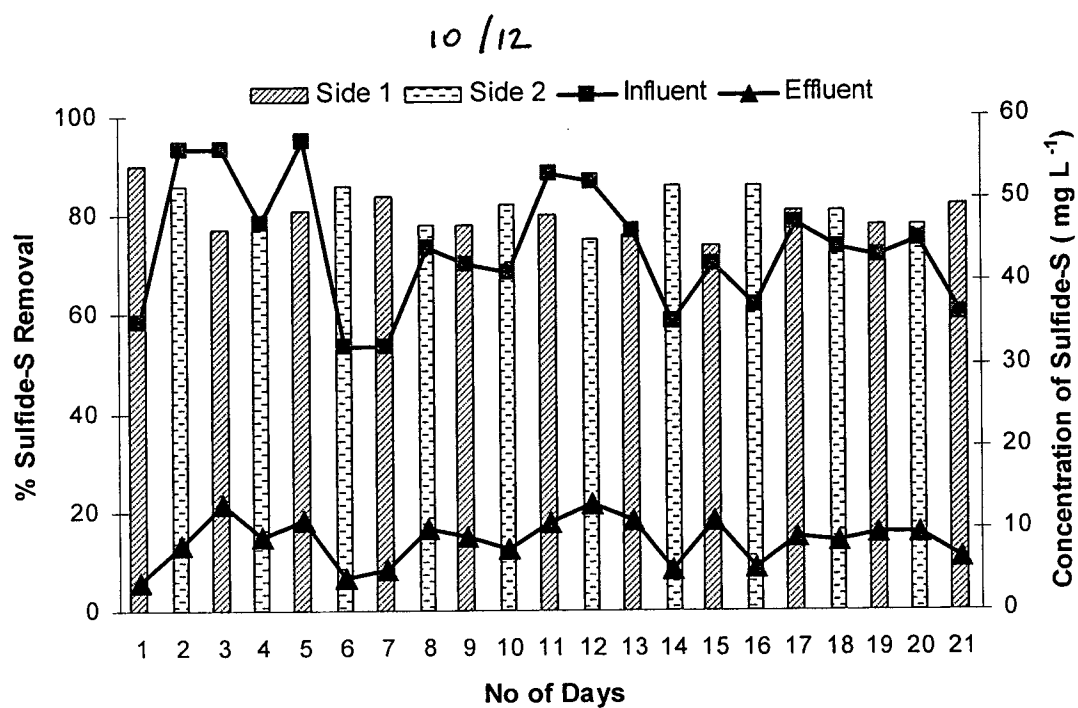


Figure 11.

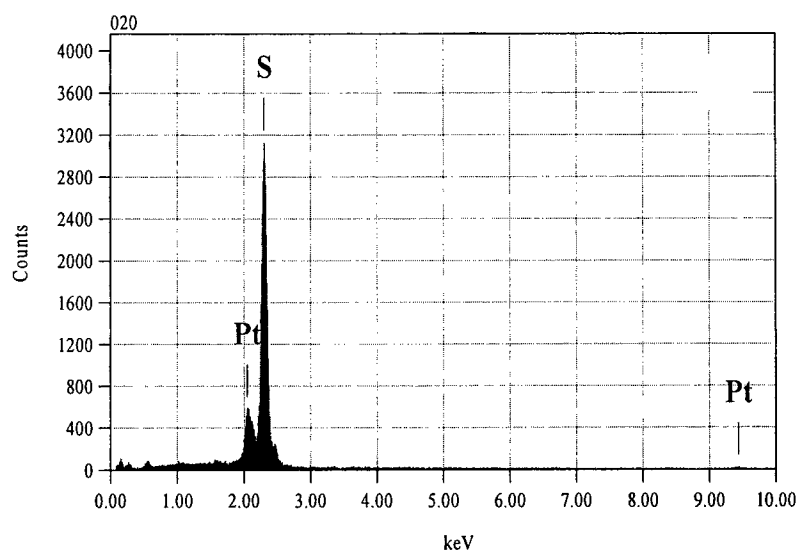
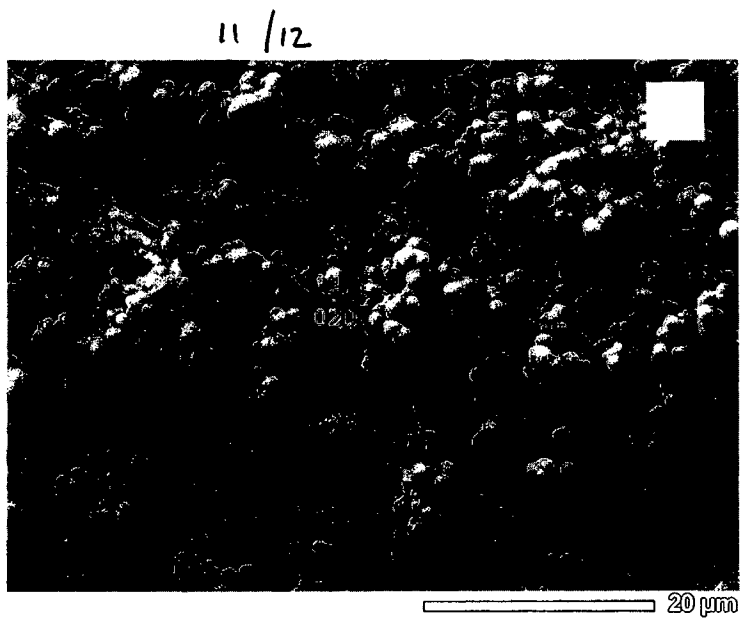


Figure 12.

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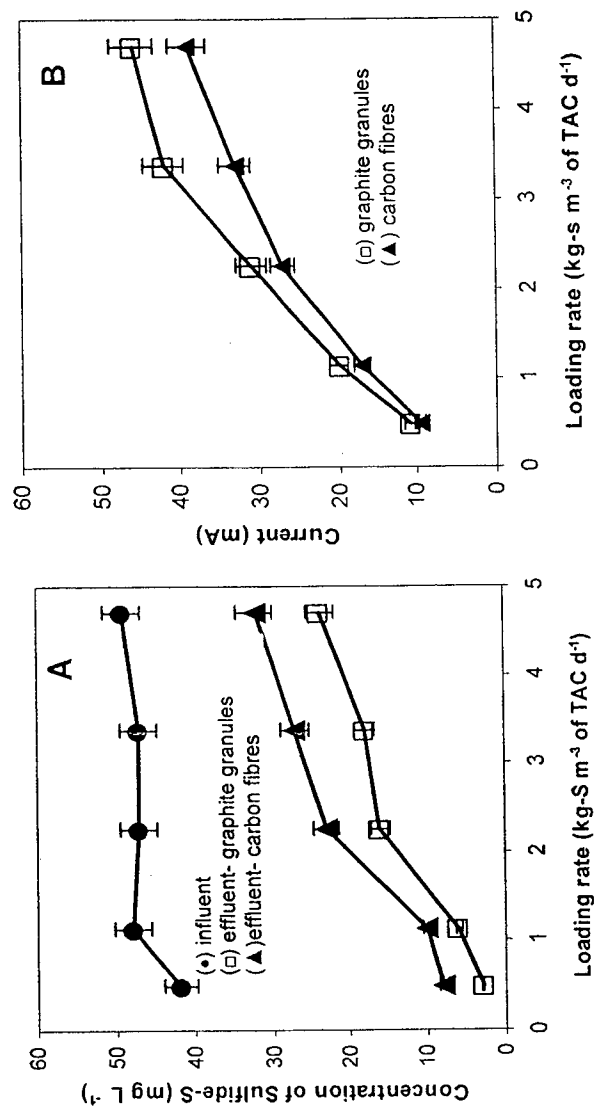


Figure 13

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2010/001649

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C02F 1/461 (2006.01)

B01D 53/48 (2006.01)

C02F 9/06 (2006.01)

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)

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 practicable, search terms used)

EPODOC & WPI: C02F 9/06, C02F 1/46/low, B01D 53/00/low & keywords (sulphide, compartment, electrode, second, third, aqueous, electrochemical, wastewater & like terms)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2009/082205 A1 (PAQUES B.V.) 2 July 2009 Abstract	1-24, 30-38
A	US 5624545 A (LANDFORS et al.) 29 April 1997 Abstract	1-24, 30-38
A	US 4765873 A (CHANG et al.) 23 August 1988 Abstract; figure; column 3, lines 1-45	1-24, 30-38

☒ Further documents are listed in the continuation of Box C☒ See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
07 February 2011Date of mailing of the international search report
08 FEB 2011Name and mailing address of the ISA/AU
AUSTRALIAN PATENT OFFICE
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2010/001649

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3409520 A (BOLMER et al.) 5 November 1968 Figure; column 1, lines 53-72; column 2, lines 47-72	1-24, 30-38
X	WO 1998/035748 A1 (SACHEM INC) 20 August 1998 Figure 3; page 30, line 27 – page 31, line 9; page 31, lines 10-13	25, 27
X	US 4308117 A (SWEENEY) 29 December 1981 Figures 2-3; column 4, lines 33-39; column 4, line 56 – column 5, line 11	25, 27
X	US 4073705 A (TORIKAI et al.) 14 February 1978 Abstract; figure; column 2, lines 20-30; column 3, lines 43-50; column 4, lines 44-65	25-29

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Supplemental Box

(To be used when the space in any of Boxes I to IV is not sufficient)

Continuation of Box No:

This international application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This International Searching Authority has found that there are different inventions as follows:

- Claims 1-24 and 30-38 are directed to a method for treating a sulphide-containing solution and a method for treating a metal phosphate-containing material. It is considered that providing an electrochemical system comprising first and second electrode compartments respectively having a first and second electrode, supplying the first electrode compartment with a sulphide-containing solution and operating the first electrode as an anode, subsequently operating the first electrode as a cathode and operating the second electrode as an anode and feeding the sulphide-containing solution to the second electrode compartment, and subsequently operating the first electrode compartment as an anode, wherein a cathode solution containing sulphide or polysulphide of enhanced concentration is obtained, comprises a first distinguishing feature.
- Claims 25-29 are directed to an electrochemical system. It is considered that a system comprising a first, second and third electrode compartments respectively having a first, second and third electrode, wherein each compartment has an anode solution inlet and one or more cathode solution inlets, comprises a second distinguishing feature.

The only feature common to both groups is *an electrochemical system comprising a first and second electrode compartment, respectively having a first and second electrode, wherein each compartment has an inlet.*

However, this **common feature is generic in the art**. This means that the common feature cannot constitute a special technical feature within the meaning of PCT Rule 13.2, since it makes no contribution over the prior art.

Therefore it follows that the common feature cannot provide the necessary technical relationship between the identified inventions, and the claims do not satisfy the requirement of unity of invention *a posteriori*.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2010/001649

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	2009082205	CA	2710424	CN	101918106	EP	2237855
		US	2011011799				
US	5624545	AU	70868/94	BR	9406830	CA	2166083
		FI	956205	NZ	268111	SE	9302213
		WO	9500701				
US	4765873	EP	0226415	NO	864899		
US	3409520	NONE					
WO	9835748	AU	68974/00	AU	62721/98	CA	2380839
		CN	1247481	EP	1235752	NZ	517085
		US	5868916	US	5910237	US	5951845
		US	6217743	WO	01,10785	ZA	9801128
US	4308117	BR	8007284	CA	1159011	EP	0028925
		JP	56084486	US	4248681	US	4256552
		US	4334968				
US	4073705	JP	52049984				
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
END OF ANNEX							