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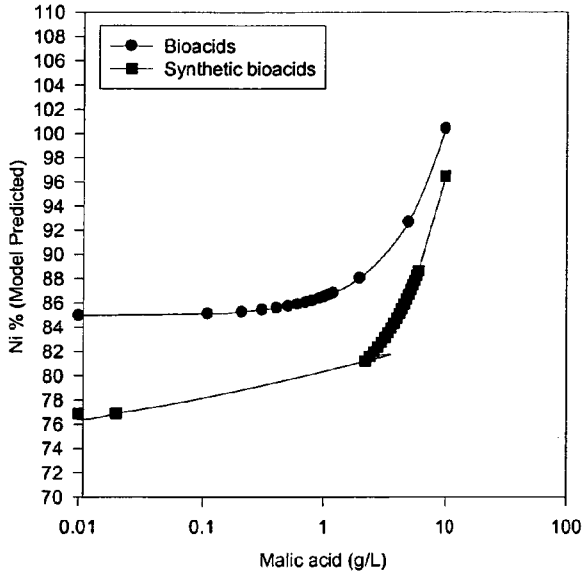


FIG 3

(57) Abstract: A process of leaching a metal value, such as nickel, from a metal laden solid, such as ore. The process includes the steps of contacting the metal laden solid with a leach solution comprising an organic bio-acid to provide a metal value containing leachate. At least the major proportion of the organic bio-acid in the leach solution is malic acid. The leachate is recovered for further processing to remove the metal value.

LEACHING PROCESS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority from AU 2008901797, which is incorporated herein in its entirety by reference.

FIELD OF THE INVENTION

The present invention relates to the leaching of a metal value from a metal laden solid using organic bio-acid. The process of the present invention is particularly, but not only, suited to the leaching of a metal value from an ore.

BACKGROUND

The removal of a metal from a solid laden with that metal can be desirable when the metal has commercial value. Ore obtained from a mine site is a metal laden solid that typically comprises one or more metal values of commercial interest. For example, laterite ore contains nickel and cobalt which are metal values that can attract a high price on the commodities market. The main uses of nickel include the production of stainless steel, rechargeable NiCad batteries and the production of electronic and computer equipment. Titaniferous magnetite ores contain metal values such as vanadium, iron and titanium, all of which are commercially desirable. Vanadium is valuable globally as an alloying agent for increasing the tensile strength and hardness of carbon steels, tool steels and high-strength and low-alloy steels. Ilmenite ore is a fraction of magnetite ore that contains titanium, which can be oxidised to titania. Titania is a valuable material in many industrial and consumer products. The major use of titania is as the white pigment in paints, plastics, and paper.

In some cases, the removal of a metal from a metal laden solid can be to improve the disposability of that solid. For example, the removal of a metal from catalyst waste can mean that the bulk catalyst (in the absence of the metal) is easier to dispose of since it no longer contains a metal that may be deleterious to the environment.

The efficient removal of a metal value from a metal laden solid has clear economical benefits. For example, the lower the removal processing costs, the higher the return on the metal value removed. Some metal laden solids comprise the metal value in a stable form or comprise very small amounts of the metal value, which can make the removal process difficult and expensive. For example, although there has been modest investment in new plant, there is widespread concern in industry about the technical and economic viability of nickel laterite processing. Laterites contain relatively low levels of nickel and cobalt and, to make matters worse, almost all reserves are impossible to concentrate, thus requiring all of the ore to be processed to extract the nickel and cobalt. Nickel laterite is also highly stable, so requires aggressive processing treatments adding further to the costs and technical difficulties. Processing all of the ore is expensive and introduces technical complexities inherent in processing large amounts of other minerals (referred to as gangue or waste) at the same time. Processes that have been used to extract vanadium involve high energy reduction roasting, salt roasting, and smelting processes. Salt roasting requires that the ore be heated to temperatures as high as 1200 °C. A number of alternative vanadium extraction methods, such as acid leaching, can be technically effective, but are costly due to high acid consumption. Current titania processing has problems of feedstock supply, cost and the generation of toxic waste. In particular, only some titanium ores are suitable as feed materials for processing. Low-grade ilmenite, the most plentiful source of titania, has little or no economic value because it is unsuitable for processing with conventional methods. Not only is the ilmenite unviable, but the opportunities for the economic recovery of other valuable minerals present in the low-grade deposit are lost.

Generally, current commercial extractions of metal values such as nickel, cobalt, iron, vanadium and titanium from ores are energy intensive and operational costs are high. Despite these difficulties, processing of ore deposits continues to grow strongly. The sustainability of the production of many metals depends upon the development of new processes that allow the vast deposits of low-grade ore in particular to be commercially exploited.

Accordingly, developments in leaching that increase metal value recovery and/or which reduce the time taken to leach the metal value from the metal laden solid are commercially desirable.

SUMMARY OF THE INVENTION

According to a first aspect of the invention there is provided a process of leaching a metal value from a metal laden solid, the process including the steps of:

contacting the metal laden solid with a leach solution comprising an organic bio-acid to provide a metal value containing leachate;

recovering the leachate for further processing to remove the metal value;

wherein at least the major proportion of the organic bio-acid in the leach solution is malic acid.

The metal value can have "value" in the form of commercial return i.e. the metal value is worth something to consumers. Alternatively, the metal value can have "value" in its advantageous removal from the metal laden solid.

The use of malic acid in the leach solution can be referred to as bio-leaching. Bio-leaching makes use of a heterotrophic micro-organism to produce an organic bio-acid which solubilises the metal value(s) from the metal laden solid and forms a complex with the metal value(s). Micro-organisms produce many organic bio-acids, including citric acid and oxalic acid. It has now been surprisingly found that malic acid can be more effective than other organic bio-acids at bio-leaching metal values from solids such as ore.

The invention is not limited to the type of metal value removed or the type of metal laden solid processed. In one embodiment, the metal laden solid is ore, preferably laterite ore, and the metal value is nickel and/or cobalt. In another embodiment, the metal laden solid is magnetite ore, and the metal value removed is vanadium. In yet another embodiment, the metal laden solid is ilmenite ore and the metal value is titanium.

Advantageously, the process further includes the step of adjusting the pH of the leach solution to below the iso-electric point of the metal laden solid to prevent or alleviate adsorption of the metal value onto or into the metal laden solid. The pH can be adjusted by using a suitable concentration of mineral acid in the leach solution.

BRIEF DESCRIPTION OF THE FIGURES

Preferred embodiments of the invention will now be described with reference to the following drawings, which are intended to be exemplary only, and in which:

FIGURE 1 is a graph showing that low oxygen reduction potential has a positive effect on nickel recovery;

FIGURE 2 is a table showing the percentage of nickel recovered from high grade saprolite ore by different amounts of malic acid (g/l);

FIGURE 3 is a graph showing the predicted percentage of nickel leached from high grade saprolite ore by different amounts of synthetic and biologically produced malic acid (g/l);

FIGURE 4 is a graph showing the predicted percentage of nickel leached from high grade saprolite ore by different amounts of synthetic and biologically produced citric acid (g/l);

FIGURE 5 is a graph showing the predicted percentage of nickel leached from high grade saprolite ore by different amounts of oxalic acid (g/l);

FIGURE 6 is a graph showing the actual percentage of nickel leached from high grade saprolite ore by different amounts of synthetic and biologically produced malic acid (g/l);

FIGURE 7 is a table showing nickel recovered from high grade saprolite ore with metabolic bio-acids comprising malic acid in excess of 60 % and sulphuric acid in 10, 20 and 30 % pulp densities;

FIGURE 8 is a table showing the recovery of vanadium from raw magnetite spinel concentrate using H_2SO_4 or HCl in combination with various concentrations of malic acid (30 % pulp density, 90 °C, 600 rpm, 6 hours);

FIGURE 9 is a table showing the recovery of vanadium and iron from Ilmenite ore sample 1 using H_2SO_4 in combination with various concentrations of malic acid;

FIGURE 10 is a table showing the recovery of vanadium and iron from Ilmenite ore sample 2 using H_2SO_4 in combination with various concentrations of malic acid;

FIGURE 11 is a table showing the recovery of titanium and iron from Ilmenite ore sample 1 using H_2SO_4 in combination with various concentrations of malic acid; and

FIGURE 12 is a table showing the recovery of titanium and iron from Ilmenite ore sample 2 using H_2SO_4 is combination with various concentrations of malic acid.

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The process of the invention is used to leach one or more metal values from a metal laden solid. In some embodiments, the process is used to leach one or more metal values from electronic waste or catalyst waste laden with metals of value. However, the process is especially suited to the leaching of a metal value from metal oxide ores. The process could be applied to oxide ores such as ilmenite which can contain appreciable quantities of titanium as well as magnesium and manganese or magnetite which contains e.g. vanadium. The present process could also be used to leach other oxide ores, for example, ore containing any of uranium, copper and gold. In one embodiment, the process is used to leach nickel from a laterite ore. The process could also be applied to ores that have similar mineralogy or chemistry to laterite ores and/or have low nickel content.

The metal laden solid is contacted with a leach solution comprising an organic bio-acid in order to leach the metal from the solid. The solid can be brought into contact with the leach solution by any means. For example, where the solid is ore, the leach solution could be

trickled onto the ore piled in a heap (i.e. heap leaching). Alternatively, the ore could be mixed with leach solution in a container in a process known as vat leaching.

The terms bio-acid, organic bio-acid and metabolic bio-acid are used herein synonymously and are intended to mean any organic acid capable of being produced microbially by a micro-organism, such as a fungus (but not necessarily so produced). Bio-acids are produced in micro-organisms via the Krebs Cycle, which is part of a metabolic pathway involved in the chemical conversion of carbohydrates, fats and proteins into carbon dioxide and water to generate a form of usable energy.

In one embodiment, the bio-acid in the leach solution is formed *in situ* in the presence of the metal laden solid. In this case, the micro-organism and the solid are combined with nutrients under conditions that encourage the production of the bio-acid. The nutrients added to the mixture can be any suitable carbon source such as sucrose e.g. molasses. In the *in situ* process, the nutrient metabolism leads to the growth of the organism and the production of the organic bio-acid metabolite in parallel with the chemical metal dissolution i.e. leaching.

In another embodiment, the bio-acid is generated *ex situ* in the absence of the metal laden solid either microbially or synthetically. The bio-acid produced in this *ex situ* process is then brought into contact with the solid.

Although the *in situ* procedure has the advantage of economising the process by achieving the fermentation and the leaching steps in the same reactor, the organisms in this system are more susceptible to abiotic stresses imposed by the toxic and corrosive environment. Selection and training of tolerant organisms are often required in the *in situ* leaching process. The *ex situ* process is preferred when the bio-acid is produced microbially because the micro-organism is not necessarily subjected to the highly acidic and toxic leaching environment and because there is more control over the specific bio-acid that is produced by the micro-organism.

At least the major proportion of organic bio-acid in the leach solution is malic acid. By "at least the major proportion" it is meant that the volume of malic acid in the leach solution is greater than the volume of any other type of organic bio-acid in the leach solution. There may be other bio-acids in the leach solution and the combined volume of other organic bio-acids may exceed the total volume of malic acid, provided malic acid is present in the largest proportion.

An example of the different amounts of bio-acids that can be present in the organic component of the leach solution can be found in the table of Figure 2.

It has been found that malic acid is particularly effective at preferentially leaching a metal value from a metal laden solid. For example, malic acid has been found to be particularly effective at leaching a metal value such as nickel from a laterite ore. This means that ores that were previously unviable (i.e. not economically viable) can be processed using the method of the present invention.

Preferably, the amount of malic acid used for leaching is at least 3 % (w/w) of the weight of the metal laden solid to be leached. It has been found that increasing the amount of malic acid in the leach solution can increase the metal recovery and in some embodiments the amount of malic acid is in the range of from 5 to 45 % (w/w) of the weight of the metal laden solid to be leached. The concentration of malic acid used in the leach solution is preferably at least 5 g/l. However, the concentration can advantageously be in the range of 1 g/l to 50 g/l, preferably 5 g/l to 20 g/l. However, these ranges could alter depending upon the amount and type of solid to be leached. The optimum amount of malic acid used for a specific solid can be tailored in the light of prior laboratory experiments.

Before being used in the process, the bio-acid (containing at least a major proportion of malic acid) is advantageously combined with a bulk mineral acid to provide a leach solution that more effectively leaches the metal value. The bulk mineral acid may be any acid known for use as a leach solution, for example sulphuric acid (H_2SO_4) or hydrochloric acid (HCl).

The primary aim of adding the mineral acid is to overcome the re-adsorption of the dissolved metals by promoting a surface charge on the solid that would repel the metal complexes in solution. Effectively, a quantity of mineral acid and bio-acid are combined in order to adjust the solution pH of the leach solution to below the iso-electric point of the solid to be leached. The iso-electric point of the solid can be determined by prior experiments. In some cases, however, it is thought that the mineral acid also provides the necessary acidity to break down or react with the solid during the leach process. In one embodiment, an equal volume of mineral acid and bio-acid can be combined to sufficiently reduce the pH of the leach solution. The mineral acid therefore supports the effectiveness of the organic bio-acid(s) in complexing with the metal components of the solid.

In one embodiment, the mineral acid is provided in concentrated form and mixed with the bio-acid(s) before the acids are diluted with water to form the leach solution.

The concentration of mineral acid used can be in the range of 50 g/l to 800 g/l, preferably 100 g/l to 300 g/l. However, this value could be more or less depending upon the amount of acid neutralising components in the solid and also upon the surface chemistry of the solid. The total amount of mineral acid required to effectively leach the metal from the solid can be referred to as the mineral acid to solid ratio (kg / kg). The mineral acid to metal laden solid ratio used can be from 0.5 to 1 to 15 : 1 (i.e. a range from 0.5 kg acid : 1 kg solid to 15 kg acid : 1 kg solid).

The amount of mineral acid required in, for example, vat leaching of ore will depend upon the required pulp density of the ore (grams of ore per 100 ml of total leach solution). For example, to effectively leach at 20 % pulp density (20 g of ore per 100 ml), 200 g/l of mineral acid is used.

In vat leaching, the pulp density can vary and values of from about 10 to 20 % provide acceptable flow rates, although lower values are possible and higher values could be used

in some cases, for example, up to 30 %. Higher pulp densities can inhibit the ability to stir and pump the material.

From an economic and environmental perspective, the less acid used in the leaching process the better. In order to lower the acid to solid ratio, salt can be added to the leach solution. Salts that can be added include, for example, sodium chloride and potassium chloride. It is speculated that the addition of salt during the leach process can further assist in reducing metal reabsorption onto the solid surface once the metal has been extracted from the molecular lattice of the solid. Accordingly, the addition of salt can reduce the amount of mineral acid required to leach metal from the solid. Salt can be added in a range of from about 1 to 2.5 wt% of the solid (although more or less could be added as desired).

As noted above, the amount of malic acid required for leaching is dependent upon the type and weight of the solid to be leached. For example, in vat leaching, this means the amount of malic acid required depends upon the pulp density of the ore. For example, with a pulp density of 2 %, only 1 to 1.2 g/l of malic acid in the leach solution may be required. At a pulp density of 10 %, 5 g/l may be required; and at 30 %, 15 g/l may be required.

However, in vat leaching, the trend for the amount of malic acid and the pulp density is not definite. Some tests undertaken in accordance with an embodiment of the present invention using nickel laterite as the metal laden solid have shown that the amount of malic acid required decreases with increasing pulp density. In one embodiment, a 20 to 30 % pulp density of high grade saporolite (HGS) ore required 12 g/l of malic acid for optimum leaching. At 10 % pulp density, the same ore required 45 g/l of malic acid to achieve a similar nickel leach. This is thought to be due to the higher pulp density reducing the oxygen reduction potential (ORP) of the leach solution. As shown in Figure 1, low ORP has a positive effect on metal recovery from HGS ore. This reflects that there may be organic components in the ore that is leached that promote lower reduction potential. This lower reduction potential appears to induce better leaching and more efficient use of the bio-acid.

As mentioned above, the malic acid in the leach solution can be produced by a micro-organism or it can be produced using other techniques. For example, using non-micro-organism routes in the laboratory, malic acid can be produced via the hydration of maleic or fumaric acid at known high temperatures and a high pressures, yielding the racemic mixture of D-(−)- and L-(+)-malic acid

Micro-organisms capable of producing bio-acids are heterotrophic micro-organisms which require organic carbon (nutrients) for growth. Fungal micro-organisms that could be used to produce malic acid include: *Penicillium (P) simplisimum, P.funiculosum, P.luterum, P.purpurogenum, P.restrictum, P.janthinellum, P.citrinum, Paecilomyces divaricatum, Mucor piriformis, Trichoderma viride, Sacharomycopsis lipolitica, Arthrobacter paraffineus, Corynebacterium sp.*, various strains of *Aspergillus (A)* and yeast genus *Candida*. The various strains of *Aspergillus* which can be used include *A.niger, A.flavus, A. wentii, A.awamori, A.foetidus, A.fenicis, A.fonsecalus, A.fumaricus, A.luchensis, A.saitoi* and *A.usumi.*

In a preferred embodiment, the bio-acid is produced by *A.niger*. To encourage preferential malic acid production, the *A.niger* can be inoculated into a suitable growth medium at a pH of about 6. Methanol (about 1 % (v/v)) can be added to improve malic acid production.

If the malic acid is produced microbially, the malic acid can be isolated from the total bio-acid produced in the Krebs Cycle by the organism. Other bio-acids that are produced include lactic, gluconic, pyruvic, succinic, ketoglutaric, oxalic, fumaric and citric acids. Alternatively, the micro-organism can be subjected to conditions that cause it to preferentially produce malic acid over other acids it can generate, for example as described above. In the latter case, the total organic bio-acid produced by the micro-organism is used as a component of the leach solution. In one embodiment, the micro-organism is subjected to conditions that cause it to produce a bio-acid having about 30 to 60 % malic acid content (in all cases malic acid is present in the highest amount among the other metabolic bio-acids).

A combination of malic acid produced synthetically and malic acid produced microbially may be used in the leach solution.

In some embodiments, the bio-acid component of the leach solution intentionally comprises malic acid in combination with another bio-acid. The potency or efficacy of the bio-acids can be controlled by selecting specific combinations of bio-acids (although malic acid is always the major proportion of the bio-acid). One effective combination includes malic acid + citric acid. Where malic/citric is the intended combination, citric acid is present in the next largest proportion following malic acid. Another combination which is particularly effective is malic acid + oxalic acid. A salt of oxalic acid could also be used, e.g. sodium oxalate. Where malic/oxalic (or oxalate) is the intended combination, oxalic acid is present in the next largest proportion following malic acid. It has been shown that malic acid in combination with oxalic acid provides improved recovery of nickel compared to either bio-acid used alone. However, preferably, when laterite ore is used in the process, the concentration of oxalic acid is less than about 7 g/l. At concentrations of greater than about 7 g/l, oxalic acid can decrease nickel recovery by forming oxalate precipitate regardless of the malic acid concentration. A further advantageous combination is malic acid + citric acid + oxalic acid.

Once an amount of metal value has been leached by the bio-acid containing leach solution, the pregnant leach solution is termed a "metal value containing leachate". The leachate can contain any amount of metal value within it before the metal loading is removed. This removal can be undertaken by any processes known in the art, including, for example, ion exchange. Optionally, the further processing is carried out immediately after the leaching step has been undertaken. Alternatively, the metal value containing leachate may be transported to another site for further processing by a third party.

EXAMPLES

Examples of embodiments of the invention will now be described with reference to the following non-limiting examples.

EXAMPLES

Example 1 – Production of malic acid

The fermentation was carried out using *Aspergillus niger*. The fungi spores were grown in Czapek yeast extract agar (CYEA) having the components listed in Table 1 below.

Table 1: Czapek Yeast Extract Agar (CYEA)

Component	g/0.25 l
Distilled water (litre)	0.25
K_2HPO_4	0.25
$NaNO_3$	0.75
$MgSO_4.7H_2O$	0.125
KCl	0.125
$FeSO_4.7H_2O$	0.0025
Sucrose	7.5
Yeast Extract	1.25
Agar	3.75
Trace Elements (ml)	0.25

*Trace elements consist of (w/v) 1% $ZnSO_4.7H_2O$and 0.5% $CuSO_4.5H_2O$

The spores grown in Czapek yeast extract agar were recovered using sodium dodecyl sulphate (0.2 %w/v). The spores were counted using a Neubauer counting chamber and typically 1 ml contains 4×10^8 spores.

2 ml of the spores were added (inoculated) to 500 ml of a sucrose based growth medium having the components listed in Table 2. The growth medium was first sterilised in an autoclave at 121 °C for 20 minutes then cooled to room temperature. The fermentation growth medium had levels of Mn below 1ppm.

Table 2: Growth medium

Component	g/l
Distilled water	1 litre
K_2HPO_4	0.128

NH_4SO_3	0.428
$MgSO_4.7H_2O$	0.25
KCl	0.428
Sucrose	150
TE (trace elements) (ml)	0.25

The pH of the growth medium was adjusted with NaOH to pH 6.0 at the point of inoculation. The medium was stirred at 100 rpm and aerated at rate of 0.5 l/min.

The pH dropped to about 2 in about two days and fermentation was allowed to proceed for another 7 to 8 days. In this process 1 % (v/v) methanol was added after 24 and 48 hours to improve malic acid production.

The bio-acids generated were analysed by Dionex ion chromatography. The malic acid was then harvested by filtration to remove any bio-mass and sterilised at 121 °C for 20 minutes, then cooled down.

Example 2 – Bio-leaching of nickel from laterite ore

HGS ore was milled to a particle size in the range of from about 80 to about 100 µm. About 0.5 : 1 to 1 : 1 (acid : ore) of sulphuric acid was added to the milled ore. Bio-acid comprising a major proportion of malic acid was added to the mixture. Three experiments were conducted using malic acid in amounts of 0.33 g/l, 1 g/l and 5 g/l. The overall concentration was adjusted with distilled water to a pulp density of about 2 %.

Additives such as salt, sodium metabisulphite were added to improve both the rate and overall leaching efficiency.

The slurry was heated to about 90 to 100 °C and stirred at about 300 rpm. Leaching was allowed to proceed for about 3 to 4 hours. After leaching was accomplished, the slurry was cooled and filtered to recover the leachate. The dissolved metals were analysed by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES).

The table of Figure 2 shows the experimental data illustrating the effect of increasing levels of malic acid on percentage nickel recovery. As malic acid is increased from 0.33 g/l to 5 g/l the percentage of nickel extracted from the ore is increased.

Example 3 – Bio-leaching of nickel from laterite ore

Figure 3 shows the predicted percentage of nickel leached (as a percentage of the total available nickel) by a leach solution comprising malic acid produced microbially (e.g. from Example 1) and malic acid produced synthetically in the laboratory. In Figure 3, relatively low levels of biologically-produced malic acid (i.e. 0.1 g/l) is predicted to leach about 85 % of the nickel from ore; however, as the concentration of malic acid increases so does the nickel recovery. The same is true for synthetically produced malic acid.

For comparison, in Figure 4 the predicted effect of leach solutions comprising various levels of synthetically and biologically produced citric acid on nickel leaching is shown. At low concentrations of biologically produced citric acid (i.e. 0.1 g/l) the amount of nickel recovered from solution is reasonably high (i.e. 85 %). The trend for citric acid remains reasonably steady at between 85 to 90 % nickel recovery even with a significant increase in the concentration of citric acid. However, metal recovery then decreases significantly as the levels of citric acid increase further. The same is true for synthetically produced citric acid. This is compared with malic acid where increasing levels of malic acid up to 10 g/l show up to 100 % nickel recovery with no reduction in efficiency at higher concentrations.

For further comparison, Figure 5 shows the predicted effect of leach solutions comprising various levels of oxalic acid. At low concentrations of oxalic acid (i.e. 2 g/l) the amount of nickel recovered from solution is reasonably high (i.e. greater than 90 %). However, similar to citric acid, the amount of nickel recovered decreases as the level of oxalic acid is increased. This is compared with malic acid where increasing levels of malic acid consistently show increased nickel recovery. The data used to generate Figures 3 to 5 is based on actual data involving leaching of high grade saprolite ore.

The low nickel recovery at high concentrations of oxalic acid is attributed to its ability to precipitate the metals from solution. The low nickel recovery at higher citric acid concentration is attributed to its lower activity at the higher citrate acid concentration. It is apparent, however, that malic acid does not demonstrate or have this high concentration restriction since nickel recovery continues to increase with increasing malic acid concentration. The implication of these trends at the higher bio-acid concentration is their impact on higher pulp densities. For economic reasons, in practice, the pulp density used will be the highest that can be practically leached: typically 10 to 30 % (although higher densities are possible). The higher pulp densities (which would have a higher solid to liquid ratio) require higher acid concentrations to effectively dissolve nickel.

Figure 6 shows actual data confirming the use of increasing concentrations of malic acid in the leach solution would have no detrimental effect on the nickel recovery. It is also apparent in Figure 6 that a leach solution comprising biologically produced bio-acid is more effective in leaching ore in comparison to the use of a leach solution comprising synthetic malic acid. This suggests that in addition to the bio-acid in the leach solution, other components produced by the micro-organism influence nickel dissolution.

An advantage of increased metal recovery with increasing malic acid concentration is that the more malic acid the micro-organism can produce, the more effective the leach solution comprising the organic bio-acid will be. This means that the biologically produced bio-acid (containing a major proportion of malic acid, and some other bio-acids) can be used in the leach solution without further processing and, when subjected to conditions that encourage it to produce malic acid, the micro-organism does not need to be monitored and controlled with respect to how much malic acid it is producing.

Example 4 – Bio-leaching nickel from a laterite ore – the effect of pulp density

HGS ore was prepared according to Example 2. The overall concentrations of samples were adjusted with distilled water to pulp densities of about 10 to 30 %.

The table of Figure 7 demonstrate that use of high concentrations of malic acid do not reduce the percentage of nickel recovery at the higher pulp densities (10 to 30 %) (as is observed with other organic bio-acids).

Example 5 - Bio-leaching of vanadium from magnetite spinel concentrate

Vanadium is considered to be associated primarily with the magnetite spinel fraction of magnetite ore where the ferric iron is replaced by vanadium i.e., $FeO.V_2O_3$ replaces $FeO.Fe_2O_3$. The titanium is contained in the ilmenite ($FeTiO_3$) fraction of the ore, which is considered to contain relatively low levels of vanadium compared to the iron based minerals. Standard extraction of vanadium from the titaniferous magnetite ore involves beneficiation to separate magnetite spinel from the ilmenite minerals. This is currently achieved by flotation and gradient magnetic separation.

The chemical composition of a magnetite spinel concentrate is shown in the Table below:

Al(wt%)	Fe(wt%)	Mg(wt%)	Si(wt%)	V(wt%)
0.52	39.375	0.02	0.61	0.484

In this Example, magnetite concentrate was milled to particle size in the range of from about 100 to about 150 µm. Sulphuric acid was added to the milled ore in different amounts ranging from 0.5 : 1 to 4 : 1 (acid : ore). Bio-acid comprising a major proportion of malic acid was added to the sulphuric acid to provide a leaching solution with an equivalent malic acid concentration of 10 g/l. The leaching solution was added to the ore to provide a slurry of 30 % pulp density.

This slurry was heated to 90 °C and continuously stirred at 600 rpm for a period of 6 hours. After leaching, the slurry was cooled and filtered to recover the leachate.

The dissolved metals in the leachate were analysed by ICP-AES. For comparison, leaching was undertaken with only sulphuric acid (1 : 1 acid to ore ratio) and HCl (4 : 1 acid to ore ratio). The results are reported in the Table in Figure 8.

The improvement in leaching of vanadium using malic acid can be seen. The effect of the changing acid : ore ratio can also be seen.

Example 6 - Bio-leaching of vanadium from un-beneficiated weathered titaniferous magnetites

The chemical compositions of two weathered ilmenite ores are shown in the Table below. The process of weathering involves the long-term exposure of the ore to air and water. This results in the oxidation and leaching of metals, specifically, the leaching of iron oxide and oxidation of FeO to Fe_2O_3. In ilmenite, the progressive leaching of iron oxide results in the concentration of TiO_2. As this occurs, the minerals become less reactive.

The extent of weathering was measured using the following:

Fe oxide that has been oxidised and leached/Fe oxide prior to weathering

= (molar TiO_2 – molar FeO)/ (molar TiO_2) *100

Metallic components	Ilmenite 1	Ilmenite 2
Extent of Weathering	71	76
TiO_2	50.7	47.7
Fe_2O_3	15.3	18.2
FeO	29.20	23.30
SiO_2	0.44	0.52
Al_2O_3	0.53	1.91
Cr_2O_3	0.24	2.12
MgO	0.9	1.17
MnO	1.27	1.93
ZrO_2	0.11	0.17
P_2O_5	0.02	0.26

V_2O_5	0.21	0.24
Nb_2O_5	0.04	0.12
SO_3	<0.010	0.04
CaO	0.02	0.08
CeO_2	<0.010	0.21
K_2O	<0.010	0.02
Na_2O	<0.009	0.05
Sc_2O_3	0.0031	0.0092

The ilmenite ores were milled to a particle size in the range of from about 150 to 180 μm. 500 g/l and 700 g/l of sulphuric acid was used in the leach solution with various quantities of malic acid. At 500 g/l the acid to ore ratio was 10 : 1. At 700 g/l, the acid to ore ratio was 14 : 1.

The slurry was heated to 100 °C and continuously stirred at 600 rpm for a period of 6 hours. After leaching, the slurry was cooled and filtered to recover the metal containing leachate. The dissolved metals in the leachate were analysed by ICP-AES.

The table of Figure 9 shows data illustrating the effect of increasing levels of malic acid on percentage vanadium and iron recovery from ilmenite ore 1. At 500 g/L H_2SO_4, the initial pH and ORP were 0.46 and 639 mV respectively. At least 15 g/l of malic acid was required to improve leaching. At 700 g/L H_2SO_4, the initial pH and ORP were -0.3 and 500 mV respectively. Only 10 g/l of malic acid was required to improve leaching.

The table of Figure 10 shows data illustrating the effect of increasing levels of malic acid on percentage vanadium and iron recovery from ilmenite ore 2. At 500g/L H_2SO_4, the initial pH and ORP were 0.32 and 567 mV respectively. Only 1 g/l of malic acid was required to improve leaching. At 700 g/L H_2SO_4 the leach efficiency was so good, the effect of malic acid could not be resolved. These results indicate that the more weathered ore has greater amenability to leaching. Mineralogically, the minerals that contain a greater proportion of TiO2, as a result of weathering are less reactive. However, the process of

weathering can also open the texture or porosity of the ores, which can contribute to improved leaching.

Example 7 - Bio-leaching of titanium from un-beneficiated weathered titaniferous magnetites

Under the same conditions, and using the same ores are in Example 6 above, titanium was leached using different concentrations of malic acid in the leach solution.

The table of Figure 11 provides data showing the effect of increasing levels of malic acid on percentage titanium recovery from the ilmenite ore 1. As shown in Figure 11, at 500 g/L of H_2SO_4 an increase in titanium extraction is not observed until 15 g/L of malic acid is used. At 700 g/L of H_2SO_4 an increase in titanium extraction is observed at 5 g/L of malic acid and higher concentrations.

The table of Figure 12 provides data showing the effect of increasing levels of malic acid on percentage titanium recovery from the ilmenite ore 2. As shown in Figure 12, at 500 g/L of H_2SO_4 an increase in titanium extraction is observed at 1 g/L of malic acid and at higher concentration.

At 700 g/L of H_2SO_4, the efficiency of leaching is significant and the effect of adding malic acid could not be observed. This experiment illustrates, however, that less sulphuric acid can be used (i.e. 500 g/l) in combination with malic acid to achieve the same effect as using more sulphuric acid (i.e. 700 g/l). The use of less acid is more economical.

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

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will

be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

CLAIMS:

1. A process of leaching a metal value from a metal laden solid, the process including the steps of:

contacting the metal laden solid with a leach solution comprising an organic bio-acid to provide a metal value containing leachate;

recovering the leachate for further processing to remove the metal value;

wherein at least the major proportion of the organic bio-acid in the leach solution is malic acid.

2. The process of leaching according to claim 1, wherein the metal laden solid is ore.

3. The process of leaching according to claim 2, wherein ore is laterite ore and the metal value is nickel and/or cobalt.

4. The process of leaching according to claim 2, wherein ore is magnetite ore and the metal value is vanadium.

5. The process of leaching according to claim 2, wherein ore is ilmenite ore and the metal value is titanium.

6. The process of leaching according to any one of claims 1 to 5, wherein the organic bio-acid component of the leach solution comprises malic acid and oxalic acid.

7. The process of leaching according to any one of claims 1 to 6, wherein the organic bio-acid component of the leach solution comprises malic acid and citric acid.

8. The process of leaching according to any one of claims 1 to 5, wherein the organic bio-acid component of the leach solution consists essentially of malic acid.

9. The process of leaching according to any one of the preceding claims, wherein the amount of malic acid in the leach solution is at least 3 % of the weight of the metal laden solid to be leached.

10. The process of leaching according to any one of the preceding claims, wherein the amount of malic acid in the leach solution is at least 5 g/l.

11. The process of leaching according to any one of the preceding claims, wherein the process further including the step of isolating the organic bio-acid from an organic bio-acid produced by a micro-organism.

12. The process of leaching according to claim 11, wherein the micro-organism is selected from *Penicillium simplisimum*, *Penicillium funiculosum*, *Penicillium luterum*, *Penicillium purpurogenum*, *Penicillium restrictum*, *Penicillium janthinellum*, *Penicillium citrinum*, *Paecilomyces divaricatum*, *Mucor piriformis*, *Trichoderma viride*, *Sacharomycopsis lipolitica*, *Arthrobacter paraffineus*, *Corynebacterium sp.*, *Aspergillus niger*, *Aspergillus flavus* *Aspergillus wentii*, *Aspergillus awamori*, *Aspergillus foetidus*, *Aspergillus fenicis*, *Aspergillus fonsecalus*, *Aspergillus fumaricus*, *Aspergillus luchensis*, *Aspergillus saitoi*, *Aspergillus usumi* and the yeast genus *Candida.*

13. The process according to any one of the preceding claims, wherein the process further includes the step of adjusting the pH of the leach solution to below the iso-electric point of the metal laden solid.

14. The process of leaching according to any one of the preceding further including the step of adding salt in a concentration of about 1 to 2.5 wt% of the ore.

15. The process of leaching according to any one of the preceding further including the step of processing the metal value containing leachate to remove the metal.

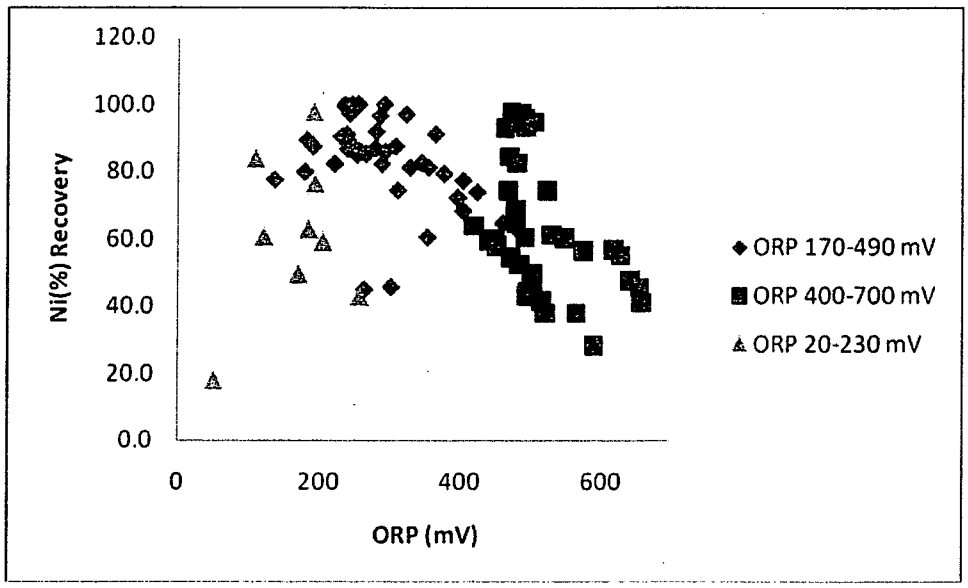

120.0
100.0
80.0
60.0
40.0
20.0
0.0
Ni(%) Recovery
0
200
400
600
ORP (mV)
ORP 170-490 mV
ORP 400-700 mV
ORP 20-230 mV

FIG 1

Pulp Density (g/l)%	pH	ORP	H2SO4 =50 g/l and Bio-acid (g/l)									Metal Recovery	
			Lactic	Gluconic	Pyruvic	Malic	Succinic	ketoglutaric	Oxalic	Fumaric	Citric	Ni%	Co%
2	0.76	511.9	0.02	0.04	0.00	0.33	0.00	0.01	0.13	0.00	0.02	72.7	51.1
2	0.66	530.90	0.02	0.04	0.00	1.00	0.00	0.01	0.13	0.00	0.02	91.7	61.7
2	0.67	546.30	0.02	0.04	0.00	5.00	0.00	0.01	0.13	0.00	0.02	94.0	58.7

FIG 2

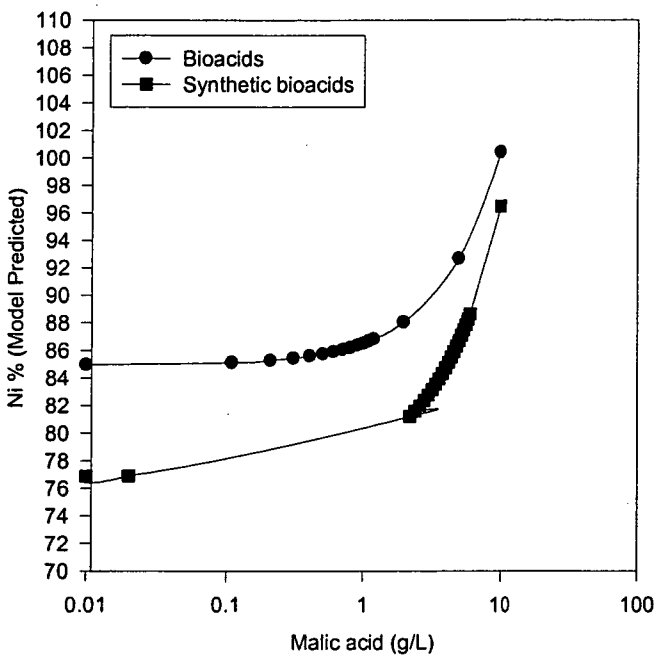

Bioacids
Synthetic bioacids
Ni % (Model Predicted)
110
108
106
104
102
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
0.01
0.1
1
10
100
Malic acid (g/L)

FIG 3

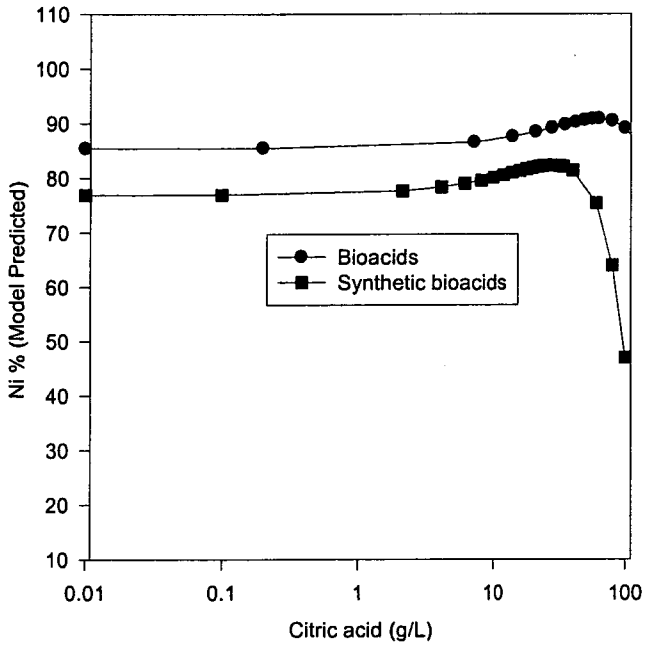

110
100
90
80
70
60
50
40
30
20
10
Ni % (Model Predicted)
0.01
0.1
1
10
100
Citric acid (g/L)
Bioacids
Synthetic bioacids

FIG 4

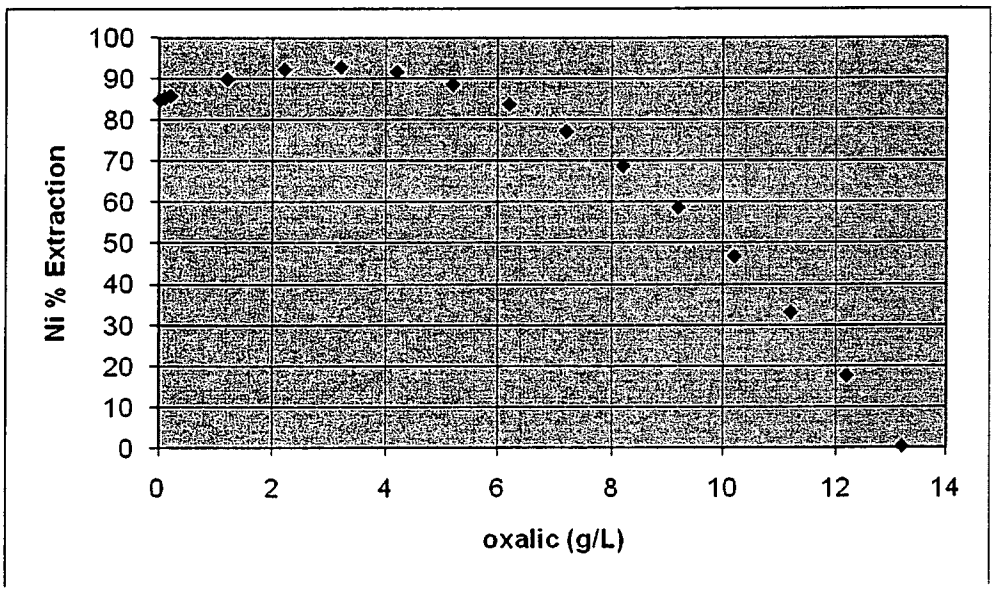

Ni % Extraction
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14
oxalic (g/L)

FIG 5

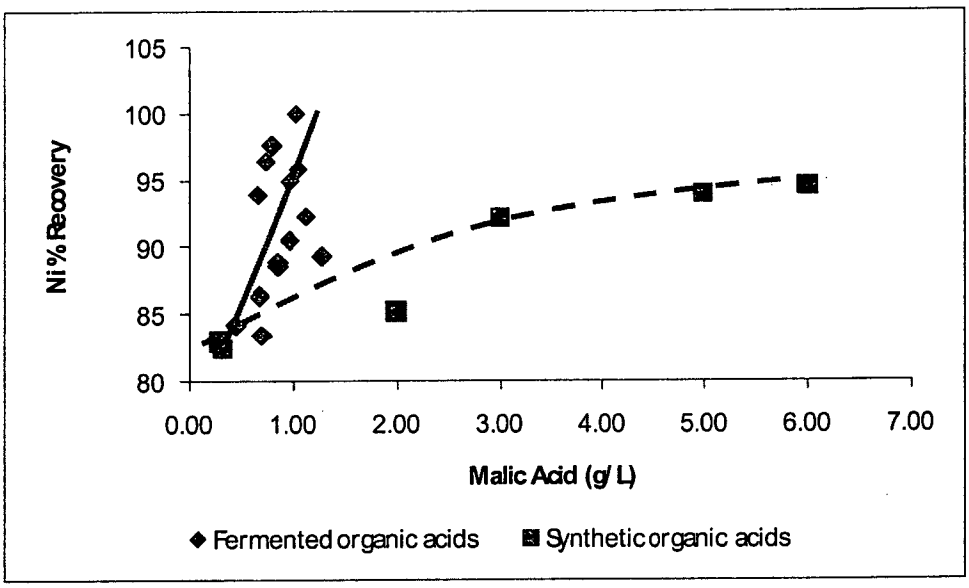

105
100
95
90
85
80
Ni % Recovery
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
Malic Acid (g/L)
Fermented organic acids
Synthetic organic acids

FIG 6

Pulp Density (g/ml)%	Malic acid (g/l)	Ni% Recovery	H_2SO_4 (g/l)
30	46	100	300
30	45	100	163
20	12	97	200
20	27	100	200
20	46	100	200
20	40	100	87
10	11	97	100
10	26	87	100
10	46	97	100

FIG 7

Leaching Reagent			Metal Recovery
Mineral acid	Malic Acid (g/L)	Mineral Acid:Ore (w/w)	V%
32 % HCl		4:1	36
98 % H_2SO_4		1:1	33
98 % H_2SO_4	10	0.5:1	37
98 % H_2SO_4	10	1:1	54
98 % H_2SO_4	10	2:1	70
98 % H_2SO_4	10	3:1	57
98 % H_2SO_4	10	4:1	36

FIG 8

H_2SO_4 (g/L)	Malic Acid (g/L)	T (°C)	Final pH	Final ORP (mV)	Metal Recovery (%)	
					Fe	V
500	0	100	0.49	342	73	71
500	5	100	0.43	360	67	63
500	10	100	0.41	355	74	71
500	15	100	0.34	356.3	81	78
700	0	100	0.05	370.4	87	86
700	1	100	0.18	361.4	82	81
700	5	100	0.06	367	88	88
700	10	100	0.01	368.3	94	94
700	15	100	0.02	356.5	100	100

Fig 9

H_2SO_4 (g/L) g/L	Malic Acid (g/L)	T (°C)	Final pH	Final ORP	Metal Recovery (%)	
					Fe	V
500	0	100	0.6	345	77	85
500	1	100	0.21	373	95.4	99
500	5	100	0.26	371	98.2	93
500	15	100	0.33	371	89.1	69
700	0	100	0.36	354.5	99.0	99.0
700	1	100	0.08	370	97.2	99.0
700	10	100	0.22	351.1	99	99.4
700	15	100	0.27	350.3	96.7	92

FIG 10

H_2SO_4 (g/L)	Malic Acid (g/L)	T(°C)	Final pH	Final ORP	Metal Recovery (%)	
					Fe	Ti
500	0	100	0.49	342	73	70
500	5	100	0.43	360	67	63
500	10	100	0.41	355	74	71
500	15	100	0.34	356.3	81	78
700	0	100	0.05	370.4	87	87
700	1	100	0.18	361.4	82	82
700	5	100	0.06	367	88	89
700	10	100	0.01	368.3	94	94
700	15	100	0.02	356.5	100	99

FIG 11

H_2SO_4 (g/L)	Malic Acid (g/L)	T(°C)	Final pH	Final ORP	Metal Recovery (%)	
					Fe	Ti
500	0	100	0.6	345	77	76
500	1	100	0.21	373	95	95
500	5	100	0.26	371	98	97
500	15	100	0.33	371	89	89
700	0	100	0.36	355	99	99
700	1	100	0.08	370	97	99
700	10	100	0.22	351	99	99
700	15	100	0.27	350	96	92

FIG 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2009/000447

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C22B 3/16 (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 and WPI: /ic/ec C22B3 and keyword(s) (malic_acid or c4h6o5 or bio_acid+), (hydroxybutanedioic or malic); EPODOC and WPI: and keyword(s) ((leach+ or elut+) and (malic_acid or c4h6o5)), ((hydroxybutanedioic or malic) and (elut+ or extract+ or leach+) and (metal+ or ore+ or cobalt or nickel or vanadium or iron or titanium)); GooglePatents and keywords "malic acid elute OR leach metal; GoogleScholar and keywords "malic acid" leaching patent metals ores.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 4414261 A1 (BURMESTER TOMAS) 26 October 1995 See abstract; and figure 1.	1-2, 6-7, 15
X	US 3958982 A (Huang) 25 May 1976 See abstract; col. 1 lines 8-11; col. 2 lines 17-59; and claims 1 to 6.	1-2, 6-7, 15
X	US 5248329 A (Rusin et al.) 28 September 1993 See abstract; col. 1 lines 36-59, col. 3 lines 1 to 36; and examples 1 to 4.	1-2, 7, 11, 15

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

* Special categories of cited documents:

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"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 May 2009	14 MAY 2009
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **JOHN DEUIS** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6283 2146

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU2009/000447

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					
DE	4414261	NONE					
US	3958982	NONE					
US	5248329	AU	15839/92	US	5221327	US	5283192
		US	5413624	WO	9214848		

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX