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(54) Title: RECOVERY OF HIGH VALUE MATERIALS FROM INDUSTRIAL WASTE

(57) Abstract: A process for isolating valuable products from low value waste including the steps of: (i)(a) leaching the low value waste, to form a leachate; (i)(b) filtering the leachate to produce a first filtrate and a first residue; (ii) carbonating the first filtrate; and (iii) precipitating one or more valuable products from the carbonated filtrate.

RECOVERY OF HIGH VALUE MATERIALS FROM INDUSTRIAL WASTE

FIELD OF INVENTION

[0001] The present invention relates to the field of generating high value materials from low value material such as fly ash derived from the combustion of brown coal (lignite), or the ash from municipal solid waste incinerators or other end products of industrial processes, or geological deposits such as clay or minerals that can be mined at low cost.

[0002] In another form the present invention relates to CO_2 sequestration by mineral carbonation reaction with waste material or low cost mineral feeds.

[0003] In another form the present invention relates to the field of recovering high value materials, particularly metals such as magnesium, from waste material.

[0004] In one particular aspect the present invention is suitable for CO_2 sequestration through formation of high value mineral carbonates from brown coal-derived fly ash.

[0005] In another particular aspect the present invention is suitable for extraction of fuel additives from clay deposits.

[0006] It will be convenient to hereinafter describe the invention in relation to recovery of magnesium metal from brown coal fly ash, however it should be appreciated that the present invention is not so limited and can be used for recovery of other materials and other metals from other industrial wastes such as incinerator ash and metal processing slag rich in alkaline earth metals and iron. The present invention can also be used for recovery of other materials and other metals from cheaply won or readily accessible geological deposits such as clay or mineral deposits.

BACKGROUND ART

[0007] It is to be appreciated that any discussion of documents, devices, acts or knowledge in this specification is included to explain the context of the present invention. Further, the discussion throughout this specification comes about due to the realisation of the inventor and/or the identification of certain related art problems by the inventor. Moreover, any discussion of material such as documents, devices, acts or knowledge in this specification is included to explain the context of the invention in terms of the inventor's knowledge and experience and, accordingly, any such discussion should not be taken as an admission that any of the material forms part of the prior art base or the common general knowledge in the relevant art in Australia, or elsewhere, on or before the priority date of the disclosure and claims herein.

[0008] Coal combustion by-products such as fly ash and CO_2 have the potential to negatively impact the environment. Fly ash can contaminate the soil and ground water, and CO_2 is a greenhouse gas that contributes to global warning. Methods to reduce the quantity of human-made CO_2 emissions have been an industrial, scientific and political focus for decades. Concerns about climate change have forced both the industrial and scientific communities to investigate possible methods for reducing CO_2 emissions from fossil fuel burning and render the use of fossil fuels as an environmentally acceptable energy source. This has led to CO_2 sequestration methods including underground injection or geological storage, oceanic storage and mineral carbonation.

[0009] Mineral carbonation involves reacting CO_2 with minerals containing metals such as Ca and Mg to form insoluble carbonate products. There are many different methods available for carbon sequestration via mineralisation. These include direct carbonation, where CO_2 gas is reacted directly with the solid, mineral containing substance to produced carbonated species, or alternatively, CO_2 is reacted with the mineral-containing substance which has been dissolved into an aqueous solution. Another method available is indirect carbonation. This is where the CO_2 gas is reacted with an aqueous solution that contains the minerals from the chosen waste substance, but the reactive components, the metal ions, have already been extracted and can more readily react with the gas to form metal carbonates

[0010] Mineral carbonation has the advantage of being exothermic (requiring no energy input and being a net producer of energy), the products are long-term storage stable and low environmental impact. Accordingly, mineralisation is currently a major research focus for industry because it can take CO_2 emissions from facilities such as coal fired power stations and react it with post coal combustion to form mineral carbonates. The attraction of these methods of carbon dioxide sequestration is that it has the potential to reduce the CO_2 emission of industry, as well as the potential to use wastes from other industrial sources to sequester the CO_2, making use of that waste rather than it also being a problem.

[0011] In the past, much of the focus of mineral carbonation research has been on minerals that have been mined for their calcium or magnesium content, such as serpentinite. Recently, the focus has moved from mined minerals to industrial waste sources containing desirable chemical species, such as calcium and magnesium oxides, which can then be extracted as ions in solution for a carbonation reaction. Such sources include the fly ash combustion waste from municipal solid waste incinerators and coal fired power stations. This is significant for a region such as the state of Victoria, Australia, which derives most of its electricity from coal burning.

[0012] For example, Victorian brown coal fly ash is a highly alkaline material that is rich in oxides, and contains relatively high proportions of CaO (29.7 wt %) and MgO (25.5 wt %). It also includes lower amounts of Fe_2O_3 (11.1 wt %), SiO_2 (9.2 wt %) and Al_2O_3 (2.5 wt %). The relatively high content of CaO and MgO make this fly ash a suitable source, as the carbonates formed will be $CaCO_3$ and $MgCO_3$, which can then be used in other industries such as the paper industry, or the manufacture of other high value products. The high content of Ca and Mg is also desired as this minimises the presence of other trace minerals which may have an effect on the carbonation of these two metal ions.

[0013] Currently approx 1.3 million tonnes per annum of fly ash is generated from Victorian brown coal combustion in the Latrobe Valley. Most fly ash is disposed of. Very little is used by industry, mainly for concrete production. Due to its high moisture content (up to 75% on the mass basis), Victorian brown coal has a much higher greenhouse gas emission rate than black coal and natural gas.

[0014] Products such as calcium carbonate, $CaCO_3$, can be used as paper filler and in paper coatings to provide opacity, high brightness and improved printability due to its good ink receptivity.

[0015] Magnesium carbonate can be thermally reduced to form magnesium metal, which is relatively high value, having a current market price of about AUD$5,000 per tonne. As a light but strong metal, magnesium is an important material in numerous industrial applications including production of alloys, particularly aluminium alloys for use in automobiles and other consumer items. It is extensively used in the automotive industry and electronic component manufacture.

[0016] Magnesium oxide and magnesium hydroxide, as precursors of magnesium metal, are also important industrial materials. In Australia, their use in the production of nickel and other metals is important. BHP Limited alone requires about 8,000 tonnes per annum. The Western Australian market for magnesium oxide is expected to be about 30,000 tonnes pa. Nearly all of the magnesium required worldwide is generated in China where the capital and operating costs are lower than most other countries and the environmental regulations are less stringent.

[0017] Magnesium hydroxide is also used in the Pigeon process, wherein it is mixed with ferrosilicon, briquetted and charged in reports made of nickel-chrome-steel alloy.

[0018] The existing processes for magnesium metal recovery utilise sea water, magnesium-rich brine, or natural mineral deposits including magnesite ($MgCO_3$) or dolomite ($CaMg(CO_3)_2$). Methods for separating the magnesium values in dolomite are described, for example in US patent 3409398 (Lloyd) and 3836627 (Wulfrafh). Methods for separating the magnesium values in magnesite are described, for example in US patent 3980753 (Grill) and US patent 3302997 (Hener). The mineral based processes are highly carbon-intensive because they require quarrying, comminution and calcinations of natural minerals. They are also very expensive due to the high cost of mineral quarrying and transportation and generate significant amounts of waste minerals during quarrying. The strip ratio (ie the quantity of waste rock to mineral), is relatively high for some open-pit mines.

[0019] Other processes for recovery of metals from fly ash, such as the electrostatic precipitation described in US patent application 2011/0251449 (Reinbek) are complex, expensive and are not directed to the recovery of magnesium or magnesium oxide and/or the consumption of CO_2.

SUMMARY OF INVENTION

[0020] An object of the present invention is to consume industrial waste of low or zero value to provide high value products.

[0021] In particular the invention aims to use fly ash, to generate high value products such as metals, or inorganic compounds such as metal oxides, hydroxides or carbonates.

[0022] A further aim of the invention is to provide a method for CO_2 sequestration.

[0023] A further aim of the invention is to provide a method for consuming both industrial waste and CO_2 to provide high value products.

[0024] A further object of the present invention is to alleviate at least one disadvantage associated with the related art.

[0025] It is an object of the embodiments described herein to overcome or alleviate at least one of the above noted drawbacks of related art systems or to at least provide a useful alternative to related art systems.

[0026] In a first aspect of embodiments described herein there is provided a process for consuming low value material to generate higher value products, the process including the steps of:

(i) leaching,

(ii) carbonation, and

(iii) precipitation

[0027] In a first aspect of embodiments described herein there is provided a process for isolating valuable products from low value waste including the steps of:

(i)(a) leaching the low value waste, to form a leachate

(i)(b) filtering the leachate to produce a first filtrate and a first residue,

(ii) carbonating the first filtrate,

(iii) precipitating one or more valuable products from the carbonated filtrate.

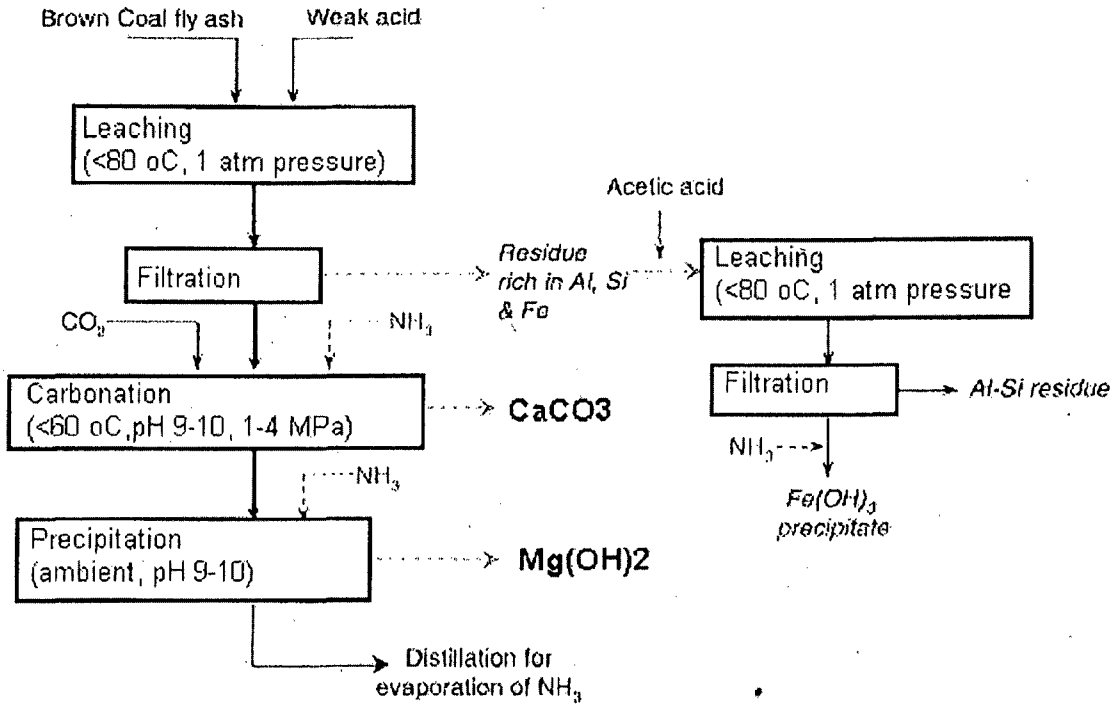
[0028] The first aspect of the process may further include the steps of:

(i)(c) leaching the first residue to produce a second leachate,

(i)(d) filtering the second leachate to produce a second filtrate and a second residue,

(i)(e) precipitating one or more valuable products from the second filtrate.

[0029] For example, when the process of the present invention is applied to fly ash, step (i) consists of a first leaching of the fly ash in a weak ammonium salt such as ammonium acetate, step (ii) consists of the subsequent capture of CO_2 through the carbonation of calcium and magnesium, and step (iii) consists of the further precipitation of magnesium as hydroxide. The used ammonium acetate can be subjected to purification and then recycled in the process. The iron in the residue of the first leaching can also be further leached (step (i)(c)), filtered (step (i)(d)) and high-purity oxide/hydroxide precipitated (step (i)(e)). Flow Chart 1 depicts the steps of the present invention using acetic acid for leaching and carbonation of brown coal fly:



Flow Chart 1

[0030] In a second aspect of embodiments described herein there is provided a process for isolating valuable products from fly ash including the steps of:

(i)(a) leaching the fly ash, to form a leachate

(i)(b) filtering the leachate to produce a first filtrate and a first residue rich in Al, Si and Fe,

(ii) carbonating the first filtrate and removing $CaCO_3$ and $MgCO_3$, and

(iii) precipitating $Mg(OH)_2$ from the carbonated filtrate.

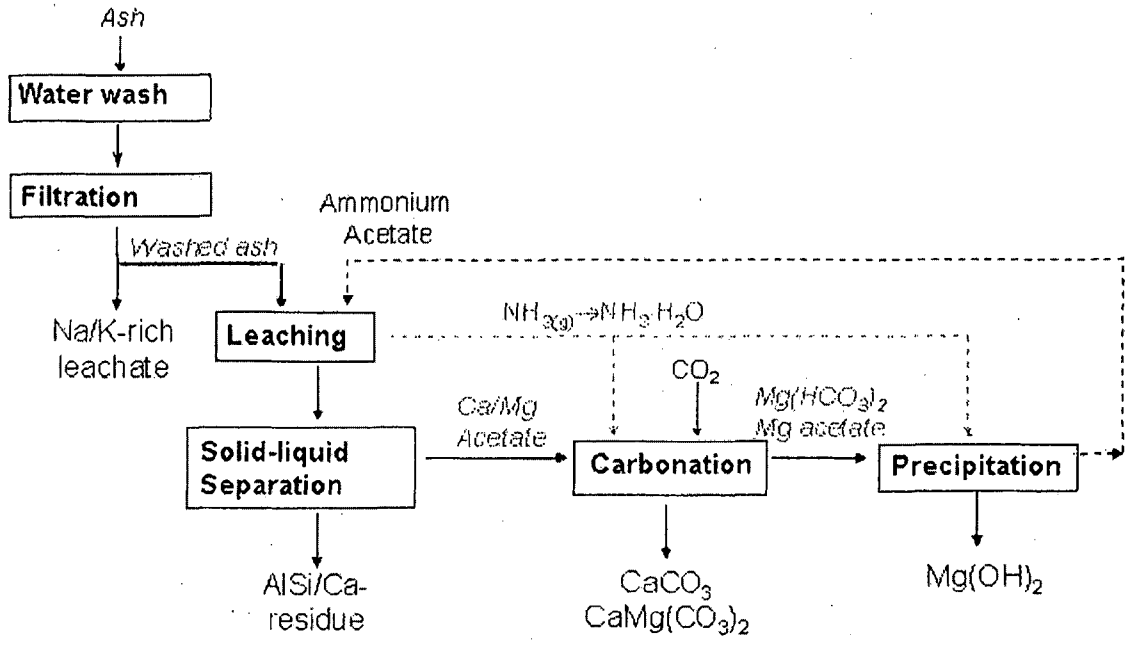
[0031] Preferably the process includes the further steps of:

(i)(c) leaching the first residue rich in Al, Si and Fe, to produce a second leachate

(i)(d) filtering the second leachate to produce a second residue rich in Al and Si and a second filtrate, and

(i)(e) precipitating $Fe(OH)_3$ from the third leachate.

[0032] A further embodiment of the present invention is depicted in Flow Chart 2 which illustrates the process of the present invention including the use of ammonium acetate in the leaching and carbonation of brown coal fly ash and steelmaking slag:



Flow Chart 2

[0033] In the leaching, the waste is typically combined with a regenerative ammonium salt, such as ammonium acetate to extract elements and produce a leachate. Typical leaching conditions would be less than about 80°C and atmospheric pressure. Ammonium acetate is particularly preferred due to its low cost and low corrosive activity. In addition, it has a high selectivity for the extraction of Ca and Mg over Fe and S. The ammonium acetate will be split into ammonium and acetate during leaching process, and these species are further combined together during carbonation process. Therefore, it can be used in a close loop with very limited consumption.

[0034] The leaching steps of the present invention may comprise multiple stages, each stage involving contacting the material to be leached with one or more fresh leachants.

[0035] Typically conditions for carbonation would be from room temperature to about 90°C, preferably less than about 80°C. Liquid to solid ratios may be in the range of from 1:1 to about 20:1, preferably about 6:1.

[0036] The carbonation pH would be adjusted using the ammonia derived from leaching process. Precipitation is typically carried out at a pH of 9 to 10 in ambient conditions.

[0037] To contribute to the sustainability of the process, typically the acid and base are recycled. For example, after carbonation using ammonia and acetic acid it is anticipated that CH_3COONH_4 may form. If so, it may be readily separated by heating to 40°C to distil off the acid and base separately (although removal of contaminant sodium and potassium ions must be addressed).

[0038] The optimal size and average particle size will differ depending on the waste material because the chemical components will differ. For example, fly ash of size 20 to 150 μm has been shown to be capable of sequestering 71.84 $kgCO_2$/ton of fly ash. This is in contrast to bulk fly ash which could sequester 56.83 $kgCO_2$/ton of fly ash, and >150 μm which could only sequester 36.47 $kgCO_2$/ton of fly ash. Fly ash of particle size <20 μm was able to sequester 62.43 $kgCO_2$/ton of fly ash.

[0039] The reaction succession for CO_2 mineral sequestration by fly ash is a simple two-step mechanism. The first reaction is the irreversible hydration of calcium/magnesium oxide:

$$(Ca/Mg)O + H_2O \rightarrow (Ca/Mg)(OH)_2 \quad \text{...equation (1)}$$

[0040] Second, is the spontaneous carbonation of the hydroxide suspensions:

$$(Ca/Mg)(OH)_2 + CO_2 \rightarrow (Ca/Mg)CO_3 + H_2O \quad \text{...equation (2)}$$

[0041] The following reactions occur with ammonium acetate. Firstly the extraction step:

$$CaO + 2CH_3COONH_4 \rightarrow Ca^{2+} + 2\ CH_3COO^- + NH_{3(g)} + H_2O \quad \text{...equation (3)}$$

[0042] Secondly, the crystallisation and precipitation steps:

$$Ca^{2+} + 2\ CH_3COO^- + CO_2 + NH_3 + H_2O \rightarrow CaCO_3 + 2CH_3COONH_4 \quad \text{...eqn (4)}$$

[0043] Thus the ammonium acetate can be fully recovered and recycled in the process.

[0044] Compared to $CaCO_3$, $MgCO_3$ is difficult to precipitate. Accordingly, it may be further precipitated as $Mg(OH)_2$ by adding extra NH_3.

[0045] As previously mentioned, the major processes of the prior art for the generation of magnesium oxide rely on the use of sea water/magnesium-rich brine, or natural mineral deposits including magnesite ($MgCO_3$) and dolomite ($CaMg(CO_3)_2$). Upgrading any of these processes to magnesium oxide involves a very complex and highly energy-intensive process. For example, sea water or brine would need to be combined with lime at a mass ratio of approximately 1:1.5 (lime to magnesium oxide), the lime accounting for two-thirds of raw material costs. The decomposition of limestone to lime represents 9 to 13% of the price of magnesium oxide, and approximately 50% of the marginal cost of production. Similarly, with respect to processes based on the use of natural mineral resources, every step of their treatment is energy-intensive. The process includes a notoriously high carbon footprint, the process involving particle comminution and calcinations. The strip ratio (the quantity of waste rock to magnesite) is also relatively high for some open-pit mines.

[0046] For the current generation rate of ~1.0 million tonnes pa and an average Mg content of 25%, there is sufficient brown coal fly ash to feed a mid-scale plant for an annual production of 100,000 tonnes $MgO/Mg(OH)_2$, which would supply the Australian market and leave two-thirds for export or for other value added applications.

[0047] In another embodiment of an aspect of the present invention there is provided a system for carrying out the process of the present invention, the system comprising

- a fly ash feed from a brown coal processing facility four use as the low value waste,

- a carbon dioxide feed from the brown coal processing facility for use in the carbonation step,

- one or more reactors for carrying out the leaching, filtering and precipitation steps, the one or more reactors being associated with the brown coal processing facility.

[0048] Other aspects and preferred forms are disclosed in the specification and/or defined in the appended claims, forming a part of the description of the invention.

[0049] The present invention is based on the use of two waste products such as fly ash and CO_2, to generate a product of higher value. This has led to the realization that waste of virtually no value, such as the fly ash from brown coal processing or incinerator waste disposal can be combined with CO_2. In essence, embodiments of the present invention stem from the realization that optimisation of the carbonation process will ensure that the maximum amount of metal ions extracted from fly ash is converted into mineral carbonates. It is from here that higher value products can be generated, such as calcium carbonate and magnesium carbonate for thermal reduction to magnesium metal.

[0050] Advantages provided by the present invention include the following:

- constructive use of low-value, or zero-value industrial waste as a feed;

- significant reduction in Australian magnesium generation process costs, improving international competitiveness;

- generation of valuable metals and other value added products;

- increased product diversification and increased income stream for the brown coal industry;

- mitigation of greenhouse gas emissions by permanent mineralisation (approximately 500 kg CO_2 being captured by one tonne of fly ash);

- relatively simple process, potentially at close to ambient conditions.

[0051] Using an industrial example of the advantages of the present invention, the State of Victoria currently produces 1.3 million tonnes/year of fly ash from brown coal. The process of the present invention could consume this fly ash to produce 247,026 tonnes of $CaCO_3$ (assumed almost pure), thus capturing 108,691 tonnes of CO2. $CaCO_3$ can be sold for $100 per tonne to the printing industry. This represents a revenue stream of $25 million (offset against the emission of CO_2 for production of acetic acid used in the process).

[0052] Furthermore, assuming implementation of a carbon tax of $25/tonne of CO_2, capturing 108,691 tonnes of CO_2 would represent a saving of $2.7 million.

[0053] Further scope of applicability of embodiments of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the disclosure herein will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0054] Further disclosure, objects, advantages and aspects of preferred and other embodiments of the present application may be better understood by those skilled in the relevant art by reference to the following description of embodiments taken in conjunction with the accompanying drawings, which are given by way of illustration only, and thus are not limitative of the disclosure herein, and in which:

Figure 1 is a plot of magnesium (1) and calcium (3) leachate concentration (g/L) against carbonation yield (%) for various leachate samples from Hazelwood brown coal mine, Latrobe Valley, Victoria. (NB: error bars present in Figure 2 are not large enough to be seen on the graphs.);

Figure 2 is a plot of carbonation yield (%) of magnesium as a result of carbonation of the optimum Hazelwood leachate at 25°C (5), 50°C (5,9,11) and 80°C (7,9,11) against volume of NH_4OH solution (mL);

Figure 3 is a plot of carbonation yield (%) of magnesium as a result of carbonation of the optimum Hazelwood leachate using 15mL (15, 19), 30 mL (13, 15, 17) and 75 mL (13, 15, 17) 28% w/w ammonia hydroxide solution at various temperatures (°C);

Figure 4 is a plot of carbonation temperature optimisation for calcium yield (%) from the carbonation of Hazelwood leachate at 25°C (21), 50°C (23) and 80°C (25) whilst varying the ammonium hydroxide solution volume (mL);

Figure 5 is a plot of calcium yield (%) optimisation for the carbonation of Hazelwood leachate using 15 mL (27), 30 mL (29) and 75 mL (31) 28% w/w/ ammonia hydroxide solution while varying the temperature (°C);

Figure 6 is a plot of the volume of ammonia hydroxide recovered (mL) from different leachates to be carbonated. The numbers next to the leachates on the x-axis indicate the length of time (in minutes) allowed for the leaching process for each of three samples identified as TE, LMG and NLMG;

Figure 7 is a plot of magnesium carbonation yield (%) for three leachates from other fly ash sources corresponding to TE (33), LMG (35) and NLMG (37), using the volume (mL) of ammonia recovered from their specific leaching;

Figure 8 is a plot of calcium carbonation yield (%) for leachates from fly ash sources corresponding to TE (33), LMG (35) and NLMG (37), using the amount of ammonia (mL) recovered from their specific leaching process;

Figure 9 is a plot of magnesium carbonation yield (%) against leachate sulphur concentration (g/L) to show the effect of the sulphur on yield for sources TE (33), LMG (35) and NLMG (37);

Figure 10 is a plot of calcium carbonation yield (%) against leachate sulphur concentration (g/L) to show the effect of the sulphur on yield for sources TE (33), LMG (35) and NLMG (37);

Figures 11(a) to 11(d) are HSC chemistry Pourbaix diagrams for an Mg-C-Ca-H_2O system at 25°C (Fig. 11(a)), at 50°C (Fig. 11(b)), at 80°C (Fig. 11(c)) and showing the previous three plots on the same axes (Fig. 11(d)). The various regions comprise MgO_2 (40), $MgCO_3$ (42), Mg(+2a) (44), $Mg(OH)_2$ (46) and MgH_2 (48);

Figures 12(a) to 12(d) are HSC chemistry Pourbaix diagrams for a Ca-C-Mg- H_2O system at 25°C (Fig.12(a)), at 50°C (Fig.12(b)), at 80°C (Fig. 12(c)) and (d) showing the previous three plots on the same axes. The various regions comprise $Ca(HCO_3)_2$ (50), Ca(+2a) (52), $Ca(OH)_2$ (54), and CaH_2 (56);

Figure 13 includes plots illustrating the proportion of calcium leached from a fly ash samples FA1 (Fig. 13(a)) and FA2 (Fig. 13(b)) measured by XRF at room temperature (60), 40°C (62), 60°C (64) and 80°C (66);

Figure 14 includes plots illustrating the proportion of magnesium leached from a fly ash samples FA1 (Fig. 14(a)) and FA2 (Fig. 14(b)) measured by XRF at room temperature (60), 40°C (62), 60°C (64) and 80°C (66);

Figure 15 includes plots illustrating the proportion of iron leached from a fly ash samples FA1 (Fig. 15(a)) and FA2 (Fig. 15(b)) measured by XRF at room temperature (60), 40°C (62), 60°C (64) and 80°C (66);

Figure 16 includes plots illustrating the proportion of various trace elements leached from FA1 measured by ICP-OES at room temperature (60), 40°C (62), and 60°C (64). The trace elements are as follows: Fig. 16(a) arsenic; Fig. 16(b)

chromium; Fig. 16(c) manganese; Fig. 16(d) zinc; Fig. 16(e) potassium; Fig. 16(f) sodium); Fig. 16(g) silicon;

Figure 17 includes XPS plots for various elements present in FA2 namely Fig. 17(a) calcium, Fig. 17(b) magnesium, Fig. 17(c) iron, Fig. 17(d) manganese, Figs 17(e) & 17(f) carbon, and Fig. 17(g) sulphur under the following conditions; room temperature 5:1 (70), 80°C 5:1 (72), room temperature 10:1 (74), room temperature 12.5:1 (76) and 80°C 1:1 (78)

Figure 18 is a plot illustrating the extraction yields of Mg^{2+} (80), and $Fe^{2+/3+}$ (82) cations out of FA2 according to a process of the present invention as illustrated by Example 3.

Figure 19 is a plot illustrating the selective extraction percentages of precipitates of $Fe^{2+/Fe3+}$ (90), Ca^{2+} (92) and Mg^{2+} (94) cations as a function of pH at 20°C of FA2 leachate to the value of 4.

Figure 20 is the XRD spectrum for the precipitate obtained from the pH 4 leachate of Example 3 including comparison traces for sodium chloride (100), haematite (102) and calcium sulphate hydrate (104).

Figure 21 is the percentages of Ca^{2+} (110) and Mg^{2+} (112) carbonated by adjusting the pH of the FA2 leachate to 11, after the selective precipitation of $Fe^{2+/3+}$ at the leachate pH of 4.

Figure 22 illustrates the extraction yields for CaO and MgO out of four brown coal fly ashes (120, 122, 124, 126) (FA1 – 122, FA2 – 124) by 4 M ammonia acetate for CaO (Figure 22 (a)) and for MgO (Figure 22 (b)).

DETAILED DESCRIPTION

Experimental

[0055] Experiments were carried out to illustrate a process for efficient use of industrial wastes and CO_2. The experiments illustrate the post-combustion metal precipitation efficiency using the indirect mineralisation method in ammonium acetate solution, while varying different experimental conditions during carbonation.

[0056] The following experiments primarily used fly ash originating from the combustion of brown coal from the Latrobe Valley, Victoria, Australia. The combustion creates two products – bottoms ash and fly ash. The fly ash escapes upwards with flue gas whereas the heavier bottoms ash collects in the bottom of the combustion reactor.

[0057] These experiments were conducted to monitor the behaviour of pure individual metals, including calcium and magnesium, as well as other trace elements, as a function of solution pH and carbonation temperature. Acetic acid was used as the leaching medium since it is easily recycled and therefore makes the process more cost effective. The carbonation pH was controlled using ammonia solution, which can also be recycled.

[0058] As the carbonation process is naturally thermodynamically favoured, thermodynamic modelling of the formation mechanisms of the different carbonates (Ca/Mg) was completed in an attempt to determine which carbonate is the most thermodynamically stable. This assisted in determining which carbonate is best suited to the storage of carbon in this form. The carbonates formed were examined using X-Ray Fluorescence (XRF) to determine their elemental and chemical compositions.

EXPERIMENT 1

Experimental method

Carbonation

1. Leachate was obtained and the leaching conditions were recorded.

2. 50ml of the leachate was measured and placed into the reactor vessel.

3. A specified amount of ammonia was added to the leachate and the initial pH and temperature were recorded.

4. A magnetic stirrer was added to the vessel and the stirrer speed was set to 175rpm.

5. Carbon dioxide was bubbled through the solution and the pH and temperature was recorded every 5 minutes for 20 minutes, while ensuring that no carbon dioxide escaped from the reactor vessel.

6. At the conclusion of the 20 minutes, the solution was filtered and the carbonate was placed in the oven for drying.

7. The volume of the filtered solution was measured and the solution was bottled, to be prepared for ICP analysis.

8. The dried carbonate precipitate was crushed into a fine powder, weighed and bottled, ready for XRF analysis.

9. Steps 1-8 were performed at room temperature with the pH being maintained between 9 and 10 for the Hazelwood leachate samples.

10. Steps 1-8 were performed at temperatures of 25°C, 50°C and 80°C and at varying amounts of ammonia solution for the optimum leachate sample.

11. Steps 1-8 were performed at room temperature with the same amount of ammonia experimentally recovered from the leaching process for the TRU Energy, LMG and NLMG leachate samples

X-Ray Fluorescence (XRF)

1. The powered carbonate precipitate samples were transferred into XRF examination cells, which were then placed individually into the XRF machine.

2. The elemental compositions of the carbonate precipitates were recorded.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

1. For each sample, 15ml of the solution was retained.

2. 1.5ml of the solution was extracted and 13.5ml of 2.5% nitric acid was added to make it up to 15ml of solution.

3. 1.5ml of this diluted sample was then extracted and again made up to 15ml by adding 2.5% nitric acid solution.

4. This process was repeated twice more to give a total of 4 serial dilutions.

5. Steps 1-4 were repeated for all leachate and filtered carbonation solutions.

6. A blank with 15ml of 2.5% nitric acid was prepared, as well as standard solutions of 500ppb, 1000ppb and 5000ppb with known intensities. These samples were used to produce a calibration curve with a correlation coefficient of 0.999.

Modelling

1. HSC Chemistry 7 was used to produce Pourbaix diagrams (also known as Eh-pH diagrams) of the magnesium and calcium ions in the carbonation solution at temperatures of 25°C, 50°C and 80°C.

2. When opening HSC Chemistry the Eh-pH diagram button was selected and selected the main element as magnesium. Calcium and carbon were selected for

the other elements and the search mode was set to Aqueous Ions. Temperatures of 25, 50 and 80 were entered for T1, T2 and T3.

3. Then pressed Ok and proceeded to select all the species that appeared in the right hand column. The file was then saved and the EpH button was clicked which opened a new window.

4. Pourbaix diagrams were produced at various temperatures by clicking on the diagram button at the bottom of the new window and the temperatures were varied by changing the selection at the top right hand of the page.

Results

[0059] Figure 1 shows that the magnesium yield from the carbonation process is constant, and close to 100%. This means that the yield from the carbonation process is independent of the leachate's magnesium concentration. This would suggest that it would be ideal to use leachates with the highest magnesium concentration possible which, given the constant high yield of the carbonation reaction, would result in a greater amount of magnesium being converted to magnesium carbonate. This would maximise the amount of magnesium carbonate produced from the process. These high magnesium concentration leachate samples corresponded to the leaching processes that have occurred for a longer period of time

[0060] Figure 1 also suggests a similar indication that the leachate samples with higher calcium concentrations should be used in the carbonation process, as they result in higher yield of calcium being extracted through precipitation. Whilst the yield is not constant for the calcium concentrations, the results suggest that higher calcium concentrations in the leachate lead to higher calcium yields after carbonation. As with the magnesium results, the higher leachate calcium concentrations correspond to the leaching processes that have occurred for a longer period of time.

[0061] As all of these carbonation experiments were performed under the same conditions, at room temperature and maintaining the pH between 9 and 10, it would suggest that the magnesium precipitated under these conditions is independent of the

initial magnesium concentration in the leachate, whereas the percentage of calcium precipitated through carbonation is higher for leachates with higher calcium concentrations. It should be noted that all of these yield were above 85%.

[0062] Figure 2 shows the magnesium yield from carbonation at 25°C, 50°C and 80°C respectively. These temperatures were chosen to examine the effect of increasing the reaction temperature on the yield of the metal. The trend observed in each of the three cases show that as the amount of ammonium hydroxide is increased, the yield of magnesium approaches 100%. Therefore it can be said that a higher amount of ammonium hydroxide leads to a higher yield of magnesium. This corresponds to the literature in the literature review, which stated that the carbonation of magnesium is favoured by higher pH values. The error bars present in Figure 2 show that the trends could quite possibly be constant rather than increasing

[0063] Figure 3 above shows the magnesium yield from carbonation with the addition of 15 mL, 30 mL and 75 mL 28% ammonium hydroxide solution. These volumes of ammonium hydroxide solution were calculated from the amount of ammonia recovered in the leaching process for the optimum leachate. These values were chosen to examine the effect of increasing the volume of ammonium hydroxide solution used, which in turn increased the pH. Calculations were required to determine the volume of 28% ammonia hydroxide solution that corresponded to the amount of ammonia recovered from the leaching.

[0064] It can be clearly seen from Figure 3 that for 15 mL of ammonium hydroxide solution, an increase in temperature leads to a decrease in magnesium yield. This trend is also present for 30 mL of ammonium hydroxide, but it is a very small reduction in yield as the temperature increases from 25°C to 80°C. For 75 mL of ammonium hydroxide, this trend seems to have disappeared altogether, with the yield remaining relatively constant across the temperatures examined. The error bars in these figures also allow for some error in the calculations and experimental measurements. They also indicate that the trends described above would hold if there were some errors in the values.

[0065] These results would suggest that using a higher temperature and as much ammonia, or ammonium solution, as is practical would be the best way to optimise this

process. This may be true in an experimental sense, but industrial practicability must be taken into account. In industry, there are always attempts to reduce energy and material consumption for the best output or production rate

[0066] These industrial goals would attempt to minimise the operating temperature of the carbonation process, as well as examining the possibility of only using the ammonia from the leaching process in the carbonation process, thus closing the "loop" of ammonia between the processes and eliminating the need to use extra ammonia in the carbonation process

[0067] With these objectives in mind, these experimental results suggest that the optimum temperature and volume of ammonium solution in an industrial sense would be at room temperature and the volume corresponding to the amount of ammonia recovered in the leaching process. This is because operating the process at room temperature means that no extra energy would be required for the process, reducing the energy costs of the reaction. Even though the magnesium yield increases with the amount of ammonia, it can be clearly seen from Figure 3 that at room temperature and with the recovered amount of ammonia that the magnesium yield is 99%.

[0068] As can be seen in Figure 3, increasing the temperature for a given amount of ammonium solution leads to a reduction in the magnesium yield at lower volumes of ammonium hydroxide. Hence, room temperature is an ideal temperature at which to operate the carbonation process

[0069] The trends seen in Figures 2 and 3 can be attributed to the thermodynamic nature of the carbonation of magnesium. As magnesium carbonation is an exothermic reaction, higher temperatures would not favour the carbonation reaction, thus leading to a decrease in the yield of magnesium. This trend is not seen when the higher volumes of ammonium hydroxide solution were used, which is due to the fact that the higher pH condition caused by the greater amount of ammonium hydroxide drives the carbonation despite the possible negative effect of the higher temperature.

[0070] The length of time to run the carbonation experiments was set at 20 minutes due to the fact that after approximately 20 minutes the pH of the solution in the reaction

vessel had dropped to approximately 7. If the pH of the solution had dropped below 7, the solution would have become acidic and the magnesium carbonate that had precipitated would have redissolved back into the solution as magnesium hydrogen carbonate. This would have had an impact on the magnesium yield achieved, and thus limiting the reaction time to 20 minutes was an attempt to reduce the amount of magnesium that redissolved back into solution.

[0071] Figure 4 shows the calcium yield from carbonation at 25°C, 50°C and 80°C respectively. The trend shown in each of the three cases is that as the amount of ammonium hydroxide is increased, the yield of calcium increases. Therefore, it can be said that a higher amount of ammonium hydroxide leads to a higher yield of calcium, but these trends are less well defined than those found for magnesium. It should be noted that in all of these experiments, the calcium yield was always above 95%, regardless of the amount of ammonium hydroxide added.

[0072] Figure 5_above shows the calcium yield from carbonation with the addition of 15 mL, 30 mL and 75 mL 28% ammonium hydroxide solution. These volumes of ammonium hydroxide solution were calculated from the amount of ammonia recovered in the leaching process for the optimum leachate. Calculations were required to determine the volume of 28% ammonia hydroxide solution that corresponded to the amount of ammonia recovered from the leaching. These calculations can be found in Appendix B.1.

[0073] It can be clearly seen in Figure 5 that for 15 mL of ammonium hydroxide solution, the calcium yield decreases with increasing temperature. Figure 6 also shows a higher yield with a higher temperature for 30 mL of ammonium hydroxide and for 75 mL of ammonium hydroxide displays a relatively constant yield over this temperature range. It can be seen that all of these yields are high, in the order of 95% and above.

[0074] What must also be noted is that the error bars displayed show that the trends could all be constant. It should be noted that these error bars seems large due to the y-axis scale, with the y-axis beginning at values in the low nineties.

[0075] These seemingly constant trends can be attributed to the calcium carbonation reaction being less sensitive to the reaction temperature then the magnesium carbonation reaction, as it is not as exothermic a reaction.

[0076] These results would suggest that the calcium yield is constantly high regardless of the process conditions being applied to the carbonation reaction. This is therefore not a problem within the scope of this project. It would, however, present a problem downstream for the carbonation process as the magnesium and calcium carbonates would have to be somehow separated.

Carbonation of leachates from other fly ash sources

[0077] As can be seen in Figure 6, different leachates produce different amounts of ammonia in their leaching process. As was done for the optimum Hazelwood leachate (above), this ammonia "loop" has also been examined for various other leachates from different fly ash sources. Figure 6 shows the different volumes of ammonium hydroxide required to close the "loop". These amounts were calculated in the same way the ammonia hydroxide solution volume was calculated for the optimum Hazelwood leachate (above). Figure 7 shows that the amounts of ammonium hydroxide recovered from the various leaching processes are not adequate for most of the leachates, as the yields produced are relatively low. The only two leachates that produce a yield comparable to that of the Hazelwood leachates are the TRU Energy 60 minute leachate, which required 6 mL of ammonium hydroxide solution and the LMG 60 minute leachate which required 12 mL of ammonium hydroxide. The purpose of investigating these leachates was to determine whether the optimum industrial conditions recommended (as above) for the Hazelwood leachates would also be applicable to these leachates. As the results suggest, the leachates with the longer leaching times produce the best yield when carbonated with the same amount of ammonium hydroxide recovered from the leaching process. This again demonstrates that longer leaching times lead to higher carbonation yields for magnesium using the amount of ammonia recovered from the leaching process, meaning no additional ammonia would need to be added in industry. The results also demonstrate, as with the conditions.

Presence of Trace Species

[0078] Figures 9 and 10 both show that a leachate with an increased sulphur concentration has a detrimental effect on both the magnesium and calcium precipitation yields from carbonation. Whilst this trend can be clearly seen in both plots, a high leachate sulphur concentration also corresponds to a low leachate magnesium and calcium concentration, as well as a low volume of ammonia recovered from the leaching. Therefore, this trend may not necessarily be the result of the sulphur presence and would require further investigation.

X-Ray Fluorescence (XRF)

[0079] X-Ray Fluorescence was used to confirm that the presence of magnesium and calcium were in the desired forms in the carbonation precipitates. This showed that the precipitates contain 25-30% magnesium and 35-45% calcium across the carbonation experiments. Higher precipitate magnesium content was seen when a higher magnesium yield was achieved.

Modelling – Pourbaix Diagrams

[0080] Pourbaix diagrams are also known as potential-pH diagrams due to the labels of the two axes. These diagrams show the predominate form in which an element will exist under a given set of environmental conditions and give a visual representation of the oxidizing and reducing abilities of the major stable compounds of an element. The vertical axis is labeled as Eh(potential) for the voltage potential with respect to the standard hydrogen potential as calculated by the Nernst equation and the horizontal axis is labeled pH for the –log function of the H^+ ion concentration. The lines of the diagram represent the equilibrium condition for that concentration of ions and variations in temperature will shift the equilibrium lines in accordance with the Nernst equation. The diagram indicates the region at which a given species will exist and thus gives a guide to the stability of a particular metal or metal oxide in a specific environment. So at any point on the diagram it can be established which is the thermodynamically most stable and theoretically most abundant form of the element for that potential and pH.

[0081] The Pourbaix diagrams of Figures 11 and 12 show the regions in which certain chemical species are thermodynamically stable. The magnesium carbonate Pourbaix diagrams show that it is stable over a pH range of approximately 3 to 12. As the carbonation reaction is favoured by high pH conditions, these diagrams provide a theoretical basis for the claim in literature that the carbonation process is favoured by a high pH, which justifies the addition of ammonium hydroxide and the need to find an optimum operating condition in regards to the amount of ammonia added

[0082] Figures 11(a), (b) and (c) show the stable compounds for magnesium at various temperatures. It can be seen that as the temperature increases, the magnesium carbonates region on the Pourbaix diagram shrinks and then disappears. This is consistent with the experimental data in Figure 11, which showed that an increase in temperature reduced the magnesium yield from carbonation. Figure 11(d) with the previous three Pourbaix diagrams superimposed on one another, demonstrates the gradual reduction in the magnesium carbonate region.

[0083] Figure 12 shows the Pourbaix diagrams for calcium at the same temperatures as in Figure 11. This shows no substantial change in the regions of stability for the species present. It is important to note that calcium carbonate is not present in these diagrams, the important species is calcium hydroxide which reacts under the carbonation conditions to form calcium carbonate. Again, Figure 12(d) is the superimposition of the other three diagrams. These results are consistent with the near constant yields obtained under various conditions for calcium

Results

[0084] The above experiment results from this research project have led to numerous conclusions regarding the carbonation reaction and the implications for the use of this process in industry. Firstly, in regards to the differing leachates, the yield of magnesium is relatively constant at the same conditions, whilst for calcium the leachates with the higher initial calcium concentration lead to the higher calcium carbonation yields.

[0085] In an attempt to optimise the carbonation yield of magnesium from the optimum Hazelwood leachate, it was found that higher volumes of ammonium hydroxide

solution and hence higher pH values lead to a greater yield. It was also found that at lower volumes of ammonium hydroxide, temperature increases lead to a lower magnesium yield, but this trend was less pronounced for greater volumes of ammonium hydroxide. Under the same conditions, it was also found that the calcium yield remained relatively constant, with changes in the temperature and ammonium hydroxide solution having small effects on the yield, which followed those that occurred in the magnesium yield. These results can be attributed to the thermodynamic nature of the reactions occurring. Other leachates from different fly ash sources were also carbonated to see if their closed "loop" would provide a sufficient yield of magnesium. Only two leachates, the TRU Energy 60 minute leachate and the LMG 60 minute leachate provided a yield large enough to be considered practical.

[0086] The experimental results were also compared to theoretical modelling in the form of Pourbaix diagrams. These diagrams showed that a high pH value favoured the formation of the metal carbonates and that at a higher temperature, the ability for a stable magnesium carbonate degraded.

EXPERIMENT 2

Experimental method

Leaching using acetic acid or hydrochloric acid (HCl)

[0087] The leaching process was undertaken using the following steps:

1. Initially a solution of 1-2 M acetic acid or HCl was produced.

2. 10g of fly ash or steelmaking slag (FA1) was weighed and the corresponding amount of acetic acid added depending on the desired liquid to solid ratio (1:1, 2:1, 2.5:1, 4:1, 5:1, 7.5:1, 10: 1, 12.5:1, 15:1, 20:1)

3. The solution was stirred gently to initiate mixing and allowed to rest for 15 mins before the pH was recorded and the flask closed to prevent acid escaping.

4. The solution was stirred for 1hr at room temperature before the pH was again measured.

5. The solution was filtered to give a leachate and a residue (for oven drying)

6. Steps 1 to 5 were repeated twice for each liquid to solid ratio at room temperature, 40°C, 60°C and 80°C.

7. The experiments were repeated for the second fly ash sample (FA2).

Leaching by ammonium acetate

1. The original fly ash obtained either in a dry (collected from electrostatic precipitator of power plant) or wet state (collected from ash pond) was first washed by water at a solid ratio of 6 for 2 hrs to remove the alkali metals (Na and K);

2. The water-washed fly ash was then mixed with 1-4 M ammonium acetate at a liquid to solid ratio of 6;

3. The mixture was transferred into a beaker where a pH electrode was also inserted in to monitor the pH variation, an inlet gas tube for air was also inserted in to achieve 2 L/min air for sparging, and an outlet gas tube for NH3 to be driven off with air together. The other end of the outlet tube is inserted into a flask containing water to dissolve the evaporated NH3 gas.

4. The beaker was transferred to a water bath with a constant temp of 80°C on the hot plate, and stirred at a speed of 300 RPM;

5. After one hr, the mixture was then filtered using a vacuum pump; the resultant leachate was save for carbonation, whereas the residue was save for analysis.

X-ray fluorescence (XRF)

[0088] Residues dried in the oven were crushed, combined with their corresponding residue from the same conditions and mixed prior to XRF analysis.

Inductively coupled plasma atomic emission spectroscopy (ICP OES)

1. Leachates from corresponding conditions were mixed and repeatedly extracted and diluted with 2.5% nitric acid solution.

2. Standard solutions of 500 ppb, 1000 ppb and 5000 ppb were prepared by analogous dilution with 2.5% nitric acid, plus a 2.5% nitric acid blank (tested to give a correlation coefficient of 0.9999).

X-Ray photoelectron spectroscopy (XPS)

Small amounts of residues were collected from FA2 for XPS analysis

Carbonation

1. Following analysis of ICP and XRF data, optimal conditions of room temperature and a liquid to solid ratio of 10:1 were determined for both FA1 and FA2.

2. Leachate pH was recorded before and after addition of ammonia

3. The solution was stirred at room temperature for 60 mins, then filtered, and the carbonate dried, crushed and weighed.

4. The above steps were repeated at the same pressure, then at 2, 3, 4, 5, 10, 15 and 20 bar.

Results

Table 1 sets out the components of the raw fly ash as determined by XRF.

Table 1:

Components	Fly Ash	
	FA1(%)	FA2(%)
Na_2O	6.58	1.01
MgO	35.8	23.0
Al_2O_3	2.60	6.98
SiO_2	5.36	11.3
P_2O_5	0.0367	0.0684
SO_3	15.1	2.63
Cl	2.14	0.149
K_2O	0.482	0.318
CaO	30.0	8.49
TiO_2	-	0.536
MnO	0.425	0.633
Fe_2O_3	11.2	43.9
SrO	0.226	0.137
BaO	-	0.863
Br	0.0332	-
ZnO	0.0270	-

[0089] FA1 has a high proportion of calcium oxide compared to FA2, and conversely, FA2 has a high proportion of iron oxide compared to FA1. Levels of magnesium are also high compared to fly ash from other countries.

[0090] Figure 13(a) is a plot illustrating the leaching of calcium from FA1 as measured by XRF. A clear trend is observed - as L/S ratio increases, the percentage leached increases. All available calcium appears to be saturated at L/S 20:1 where the graph plateaus. Table 2 sets out the T-test values from the calcium leaching (of FA1), comparing the temperature to the amount leached. All values are above 0.05 indicating that there is no significant effect on the proportion of calcium leached by using higher temperatures. Figure 13(b) is the analogous measurement for FA2. Again a clear trend is observed as L/S ratio increases, the percentage leached increases. Due to the small

amount of calcium in FA2, it is saturated at low L/S ratio, about 2.5:1. Again there is no benefit of increasing temperature to the percentage of calcium leached.

Table 2:

T-Test	P-value
Room temperature & 40°C	0.881151295
Room temperature & 60°C	0.315965997
Room temperature & 80°C	0.350359438
40°C & 60°C	0.102321365
40°C & 80°C	0.069997684
60°C & 80°C	0.896842834

[0091] Figure 14(a) is a plot illustrating the leaching of magnesium from FA1 as measured by XRF. A clear trend is observed as the L/S ratio increases, the percentage leached increases. This plateaus around 12.5:1 as the magnesium becomes saturated. It is clear without t-tests that there is no temperature effect on the proportion leached. Figure 14(b) shows analogous results for FA2. Again a clear trend is observed as L/S ratio increases, the percentage of magnesium leached increases. The magnesium is saturated at L/S ratio 7.5:1. From observation there is no benefit of a higher temperature on the percentage leaches. (The raised point on the room temperature curve at L/S ratio 5:1 is an anomaly due to human error.)

[0092] Accordingly the optimal L/S ratio appears to be around 12.5:1 where a leaching ratio of around 40% is seen. It is also noted from the room temperature curve that all available calcium is saturated at a 50% leaching rate. From previous work it is known that calcium interacts with silicon to form stable structures, thus not all of the calcium is available for leaching. As there are many elements within fly ash, it is likely that calcium forms complex interactions with these elements. As a result only about 50% of the calcium is available for leaching. This is further extended to magnesium leaching in FA1 where leaching is maximised at 80% for all temperatures and plateaus at this value soon after a 10:1 L/S ratio. Without wishing to be bound by theory it is assumed the other 20% of magnesium has formed highly stable structures that are unable to be broken down by the weak acetic acid and low temperatures.

[0093] The magnesium leaching curves for FA1 were almost identical, indicating the accuracy of the results. It is clear from observation that there is no effect of temperature on the final temperature leached. Much like calcium the optimal L/S ratio was 12.5:1.

[0094] Despite temperature having no effect on the final percentage leached it is not known whether it plays a role in the kinetics of the reaction. It is possible that at higher temperatures the elements are leached to their saturation point after a significantly less time than at lower temperatures. Despite optimal L/S ratios of 12.5:1 for both calcium and magnesium, it was the iron that determined the optimal L/S ratio.

[0095] Figure 15(a) is a plot illustrating the leaching of iron from FA1 as measured by XRF. Virtually no iron is leached up to a L/S ratio of 10. At this point leaching increases steadily. It is clear that temperature has no effect on the leaching of iron. Figure 15(b) shows the results of analogous testing for FA2. The iron appears to be saturated at an L/S ratio of 5:1. Values from t-tests (Table 3) show significance in the values between room temperature and 80°C. However there was no significance between any other temperatures indicating that there is no benefit of raising temperature on the percentage leached.

[0096] Table 3 includes T-test values from iron leaching (FA2) comparing the temperature to the amount leached. Only one value was below 0.05. However, all other values were above 0.05, indicating that this vale was a human error and in fact, there is no benefit of a higher temperature on leaching of iron from FA2.

Table 3:

T-Test	P-value
Room temperature & 80°C	0.041706903
Room temperature & 40°C	0.255006972
Room temperature & 60°C	0.355677589
60°C & 40°C	0.741034573
60°C & 80°C	0.195863948
40°C & 80°C	0.332066177

[0097] In summary, as can clearly be seen from the graphs L/S ratios of 5:1, 7.5:1 and 10:1 had virtually no leaching of iron, thus a clear leachate. Beyond these L/S ratios the iron leaching rises rapidly. The 10:2 L/S ratio was particularly sensitive for iron. As it was known that iron would spoil the final carbonate product minimal leaching of iron was required for the leachate. Thus, an optimal L/S ratio of 10:1 was chosen as clear leachate was produced. Room temperature was chosen as temperature had no obvious effect on leaching percentage.

[0098] The content of calcium in FA2 is around one third that of FA1. As a result, the maximum leaching of calcium occurs around 7.5:1 at an 80% leaching level. About 20% of the calcium is unavailable to be leached for the reasons explained above. This is despite increasing the L/S ratio or increasing the temperature. Much like FA1, there is no effect of temperature on the final percentage leached however, it may play a role in the rate of leaching. Unlike FA1, magnesium leaching from FA2 was only able to reach a maximum of 60%. The other 40% of magnesium most likely forms stable structures that are unable to be displaced by the acetic acid or low temperatures. This was achieved at a liquid to solid ratio of 7.5:1.

[0099] Iron oxide is easily corroded by acid. As a result at a 2.5:1 ratio, up to 40% leaching of iron is achieved. The high content of Fe_2O_3 in FA2 is unique and not observed for fly ash from any other source worldwide.

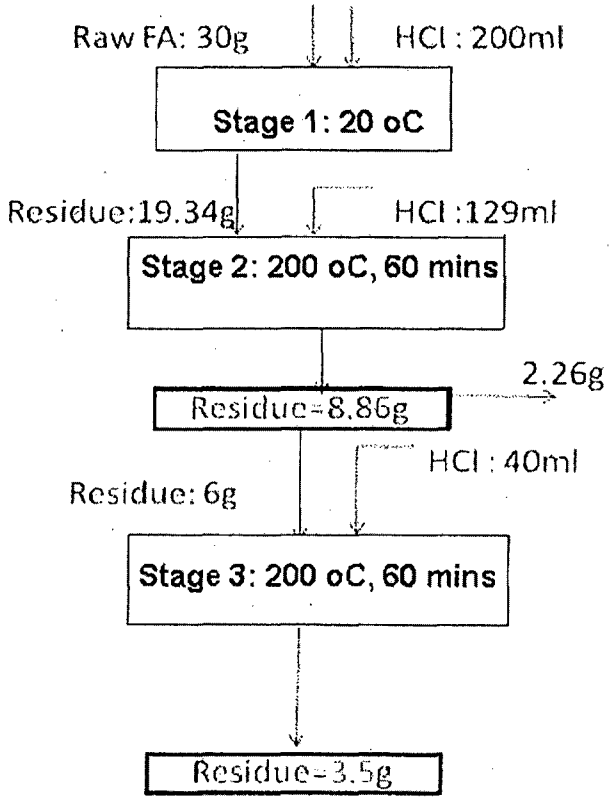
[0100] Figure 16 illustrates the proportion (in ppb) of various elements leached from 20g of fly ash (FA1) measured by ICP OES, the trace elements being as follows: Fig.16(a) arsenic; Fig.16(b) chromium; Fig.16(c) manganese; Fig.16(d) zinc; Fig.16(e) potassium; Fig.16(f) sodium); Fig.16(g) silicon). Potassium and sodium are easily leached from the fly ash, and are saturated at a L/S ratio of 5:1 and the acid dilutes them from this point onwards. Most of the trace elements reached maximum leaching at an L/S ratio of about 10:1, or spikes or starts to leach about this point.

[0101] Figure 17 illustrates XPS plots for various elements in FA2 for a range of conditions, the elements being as follows: Fig. 17(a) calcium; Fig. 17(b) magnesium; Fig. 17(c) iron; Fig. 17(d) manganese; Figs 17(e) & 17(f) carbon; and Fig. 17(g) sulphur. The carbon curves are important for standardising the other curves – as a shift of 4eV to the

right was observed, 4eV had to be subtracted off all peaks in order to determine their corresponding compounds from the NIST database. The peaks were observed to see which were decreasing so the compound(s) being leached could be determined, as well as the stable structures, which maintain their peak heights. Notably clear peaks can be observed in Fig. 17(a) at 351.5 eV for calcium (CaO); in Fig. 17(b) at 54.4 eV and 59.4 eV for magnesium (MgO and $MgAl_2O_4$); in Fig. 17(c) at 715.5 eV and 728 eV for iron (Fe_2O_3); in Figs 17(e) & 17(f) at 288.3 eV for carbon; and in Fig. 17(g) at 156.7 eV and 173.2 eV for sulphur (probably $ZnSO_4$, K_2SO_4 and $NiSO_4$). No peaks were observed in Fig. 17(d) in relation to manganese.

EXPERIMENT 3

[0102] Experiments using HCl were also conducted to improve the extraction yield of magnesium and iron from the leaching of FA2 (Yallourn coal fly ash) which is rich both magnesium oxide and iron oxide as recorded in Table 1. To improve the extraction yields of magnesium and iron from the stable ferrite matrix in FA2, a three-stage leaching procedure was employed as indicated in Flow Chart 3.



Flow Chart 3

[0103] The residue from a first-stage leaching process mentioned above was further mixed with fresh acid and subjected to the leaching autoclave for treatment. Flow Chart 3 summarises the treatment results for the mass of fly ash FA2 after three steps. By this method, the raw fly ash was dissolved efficiently, with the mass dropping from original 30 g to 19.34 g after the first stage leaching, 6 g after the second stage leaching and 3.5 g after the third stage.

[0104] Figure 18 illustrates the extraction yields of Mg^{2+}, and $Fe^{2+/3+}$ cations out of the FA2. Figure 19 shows the improvement on the extraction yields of MgO and Fe_2O_3 up to about 85% after the third stage, relative to 47% for MgO and 32% for Fe_2O_3 after the first stage.

[0105] Following the successful extraction of both MgO and Fe_2O_3 out of FA2 fly ash matrix, the pH of the resulting leachate was adjusted by addition of NaOH in order to separate Fe and Mg. Figure 19 illustrates the selective precipitation of Fe2+/Fe3+, Ca2+ and Mg2+ cations achieved by adjusting the pH to 4. Figure 19 also confirms the precipitation of around 70% of the $Fe^{2+}/^{3+}$ cation at this pH, whereas the precipitation of Mg^{2+} and Ca^{2+} is minimal. The resulting precipitate at pH 4 is rich in hematite, as confirmed by the XRD spectrum of Figure 20. Most of the dissolved Mg^{2+} remains in the leachate, >90% of which was precipitated as carbonate at the pH 11 (see Figure 21), following the methods for carbonation mentioned previously.

[0106] The experiments also confirmed the feasibility of using ammonium acetate for the leaching of calcium and magnesium out of fly ash. As shown in figure 22(a), for four different fly ashes tested, the Ca extraction yield can reach up to 60% in 1 hr, whereas the Mg extraction yield reaches up to 70%. This proves the closed loop for this whole leaching-carbonation process.

[0107] While this invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification(s). This application is intended to cover any variations uses or adaptations of the invention following in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to

which the invention pertains and as may be applied to the essential features hereinbefore set forth.

[0108] As the present invention may be embodied in several forms without departing from the spirit of the essential characteristics of the invention, it should be understood that the above described embodiments are not to limit the present invention unless otherwise specified, but rather should be construed broadly within the spirit and scope of the invention as defined in the appended claims. The described embodiments are to be considered in all respects as illustrative only and not restrictive.

[0109] Various modifications and equivalent arrangements are intended to be included within the spirit and scope of the invention and appended claims. Therefore, the specific embodiments are to be understood to be illustrative of the many ways in which the principles of the present invention may be practiced. In the following claims, means-plus-function clauses are intended to cover structures as performing the defined function and not only structural equivalents, but also equivalent structures.

[0110] It should also be noted that where a flowchart is used herein to demonstrate various aspects of the invention, it should not be construed to limit the present invention to any particular logic flow or logic implementation.

[0111] "Comprises/comprising" and "includes/including" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof. Thus, unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', 'includes', 'including' and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

CLAIMS

1. A process for consuming low value waste to generate higher value products, the process including the steps of:

(i) leaching,

(ii) carbonation, and

(iii) precipitation.

2. A process for isolating valuable products from low value waste including the steps of:

(i)(a) leaching the low value waste, to form a leachate

(i)(b) filtering the leachate to produce a first filtrate and a first residue,

(ii) carbonating the first filtrate,

(iii) precipitating one or more valuable products from the carbonated filtrate.

3. A process according to claim 2 which further includes the steps of:

(i)(c) leaching the first residue to produce a second leachate,

(i)(d) filtering the second leachate to produce a second filtrate and a second residue,

(i)(e) precipitating one or more valuable products from the second filtrate.

4. A process according to claim 1 wherein the low value waste is chosen from the group comprising brown coal fly ash, black coal fly ash, metal processing slag, incinerator waste ash or combinations thereof.

5. A process according to claim 1 wherein the higher value product is a metal or inorganic compound.

6. A process according to claim 1 wherein the step of leaching the low value waste comprises multiple stages, each comprising contacting the low value waste with one or more leachants.

7. A process according to any of the preceding claims wherein one or more chemicals are used in the process are recyclable.

8. A process for isolating valuable products from fly ash including the steps of:

(i)(a) leaching the fly ash, to form a leachate

(i)(b) filtering the leachate to produce a first filtrate and a first residue rich in Al, Si and Fe,

(ii) carbonating the first filtrate and removing $CaCO_3$, and

(iii) precipitating $Mg(OH)_2$ from the carbonated filtrate.

9. A process according to claim 8 which includes the further steps of:

(i)(c) leaching the first residue rich in Al, Si and Fe, to produce a second leachate

(i)(d) filtering the second leachate to produce a second residue rich in Al and Si and a second filtrate, and

(i)(e) precipitating $Fe(OH)_3$ from the third leachate.

10. A process for isolating valuable products from fly ash including the steps of:

(i)(a) leaching the fly ash, to form a leachate

(i)(b) filtering the leachate to produce a first filtrate and a first residue rich in Al, Si and Ca,

(ii) carbonating the first filtrate and removing $CaCO_3$, and $CaMg(CO_3)_2$

(iii) precipitating $Mg(OH)_2$ from the carbonated filtrate.

11. A process according to claim 10 wherein the step of precipitation includes subjecting the first filtrate to $Mg(HCO_3)_2$ and Mg acetate in the presence of ammonia.

12. A process according to claim 10 including recycling at least one acid and at least one base.

13. A system for carrying out the process according to claim 1, the system comprising:

- a feed of low value waste from an industrial facility,
- a carbon dioxide feed from the industrial facility for use in the carbonation step,
- one or more reactors for carrying out the leaching, filtering and precipitation steps, the one or more reactors being associated with the industrial processing facility.

14. A system according to claim 13, wherein the industrial facility is a brown coal processing facility, the low value waste is fly ash and the higher value product is one or more species chosen from the group of inorganic compounds comprising Al, Si, Ca or Mg.

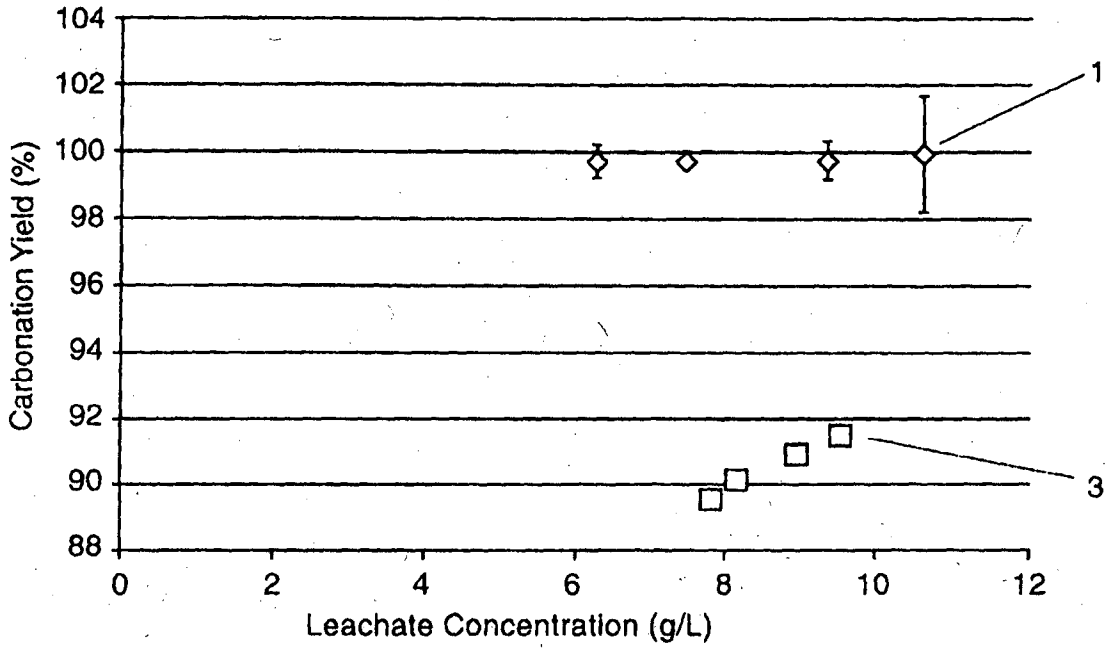


Figure 1

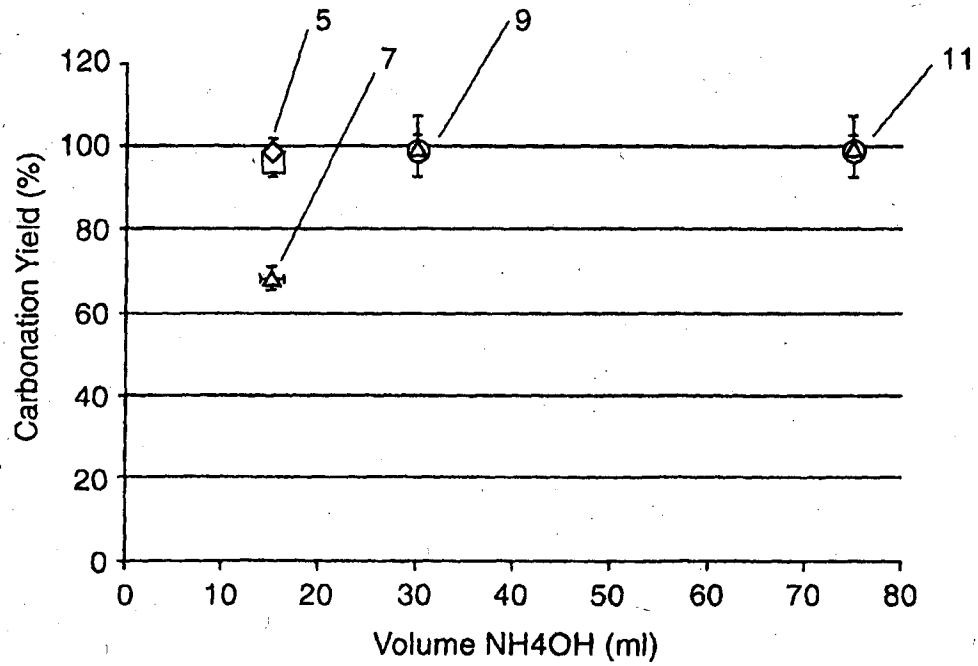


Figure 2

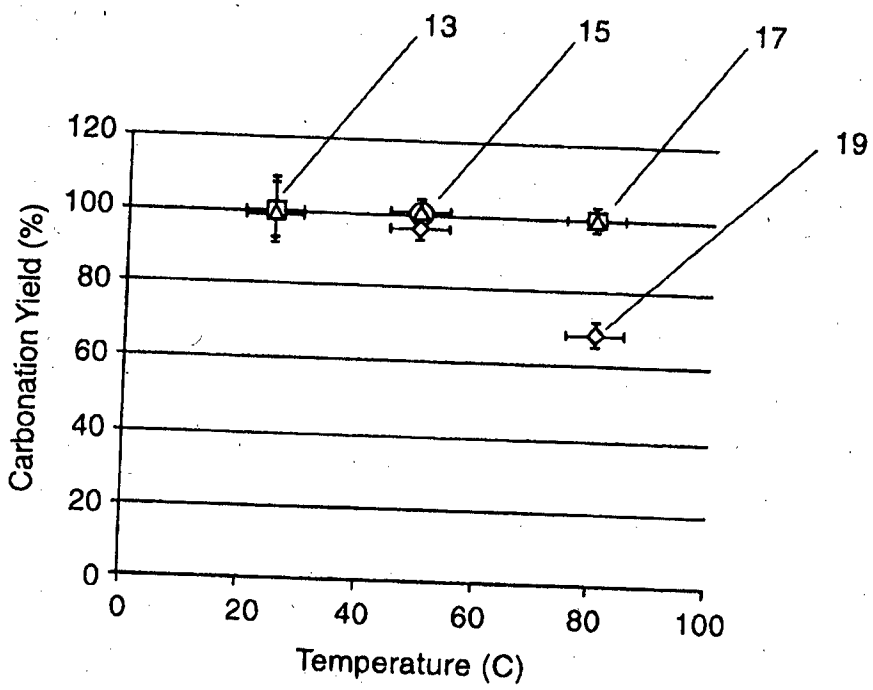


Figure 3

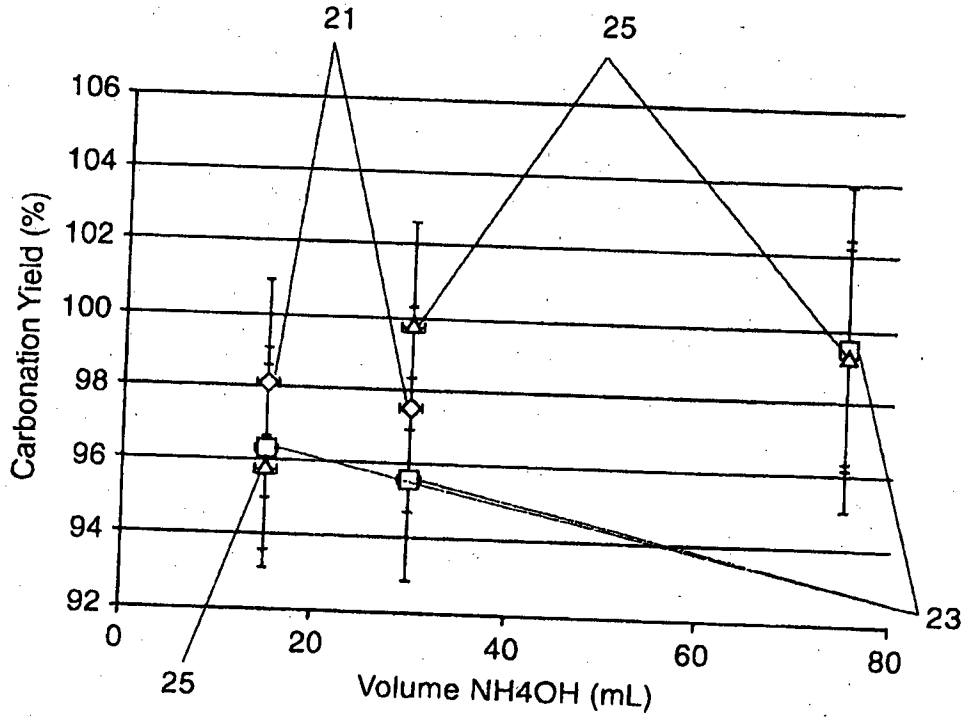


Figure 4

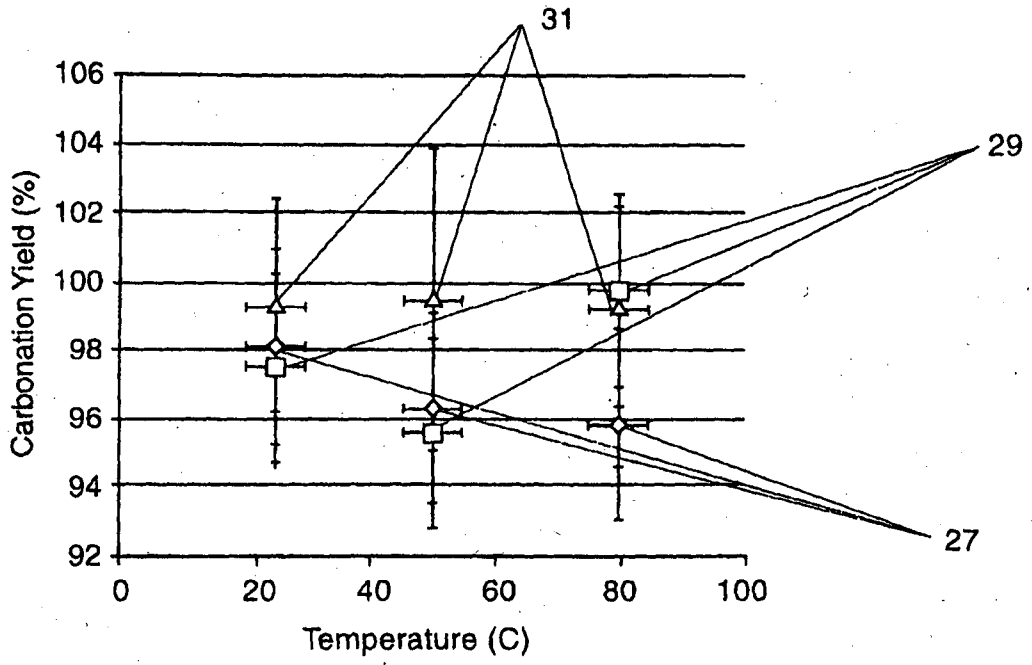


Figure 5

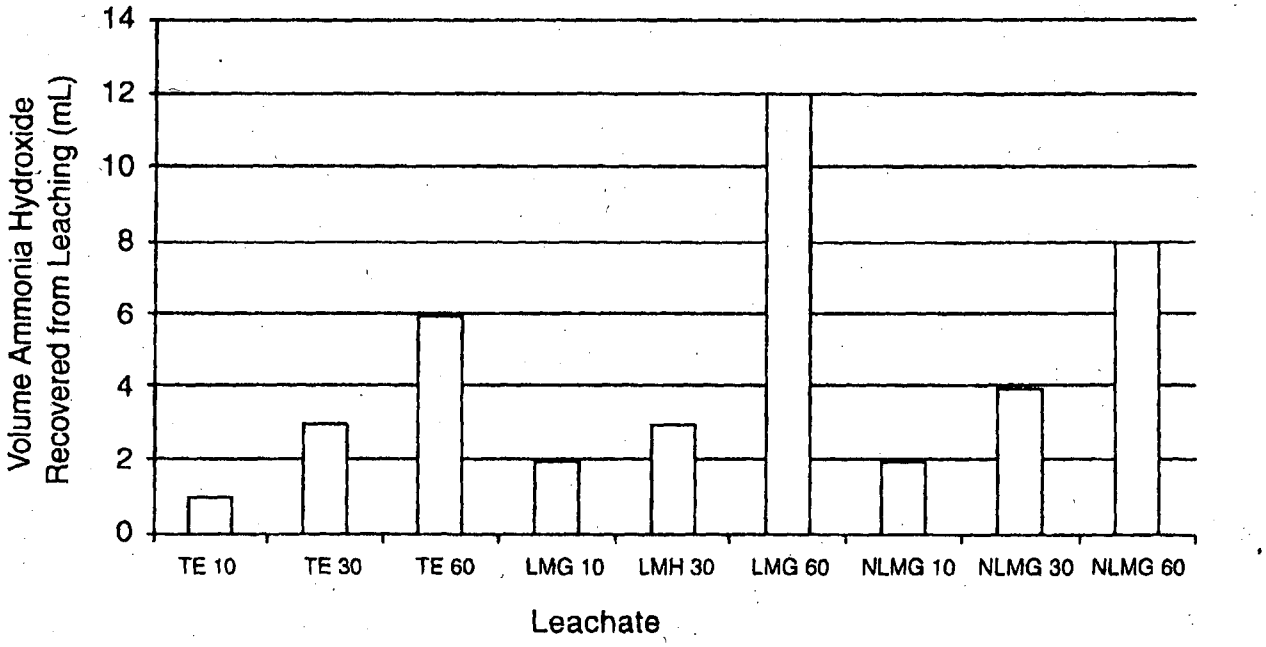


Figure 6

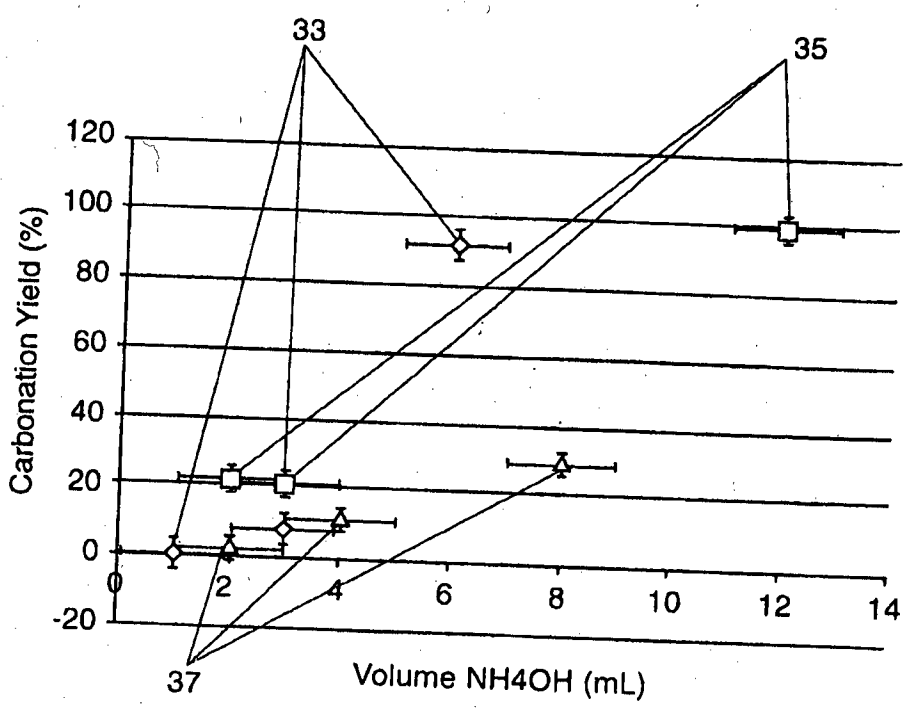


Figure 7

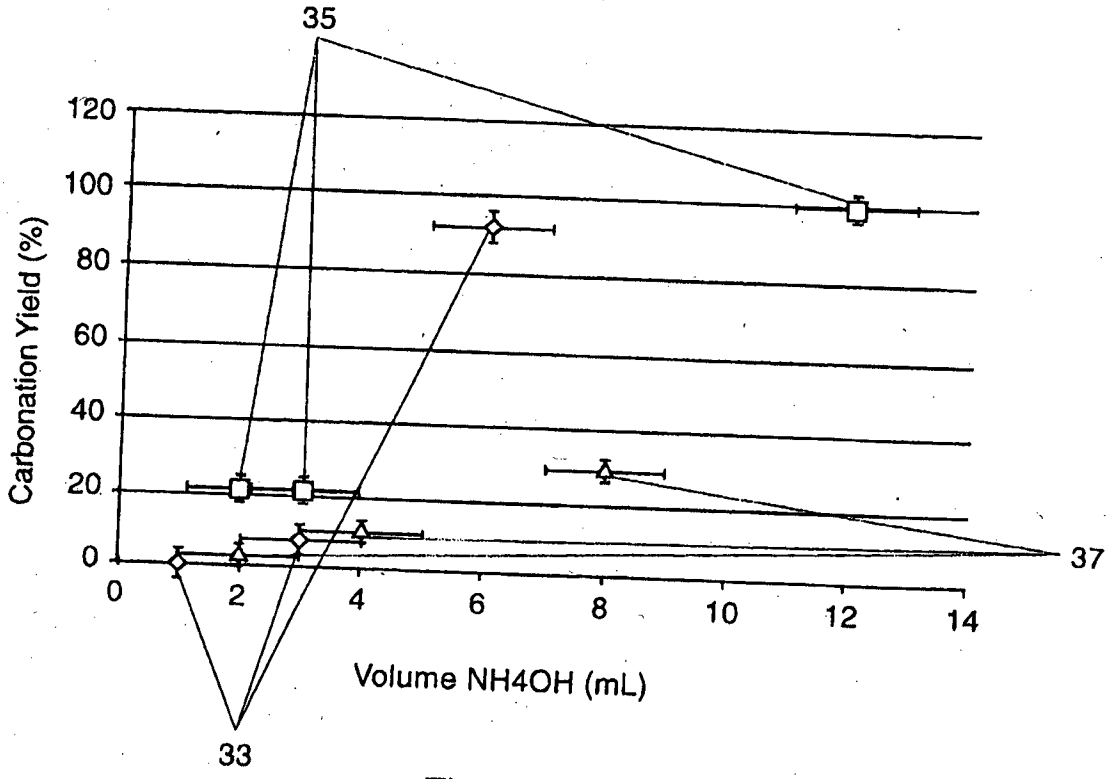


Figure 8

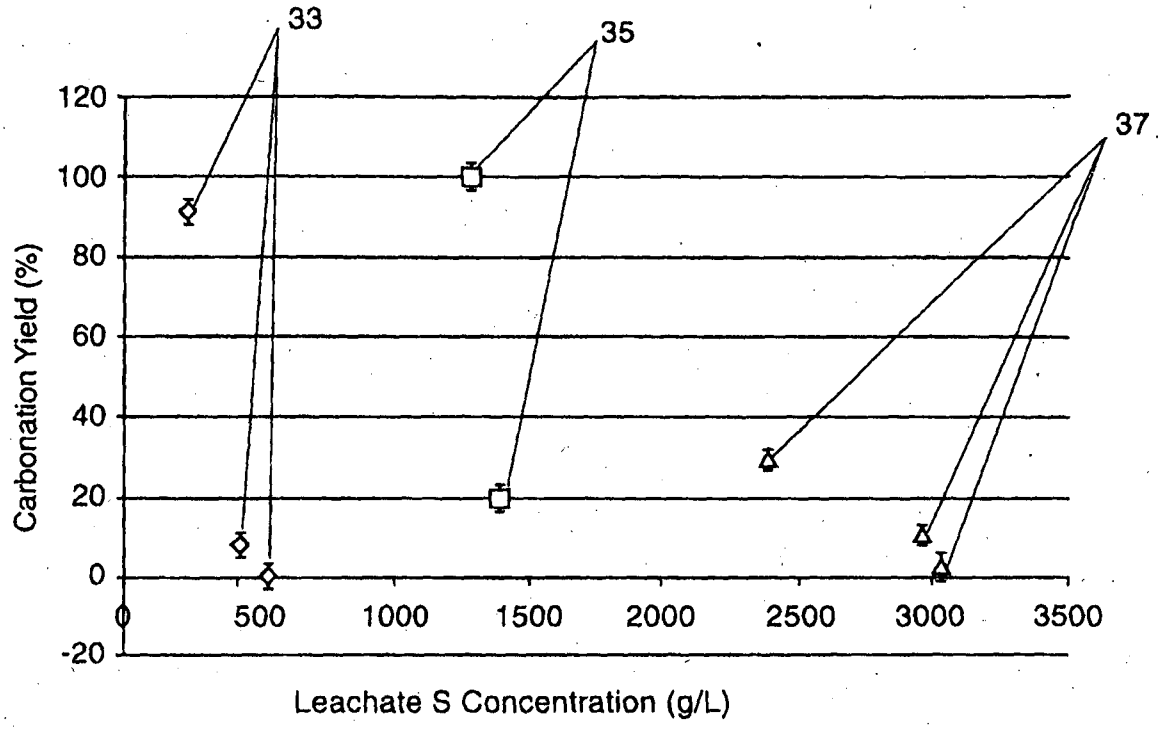


Figure 9

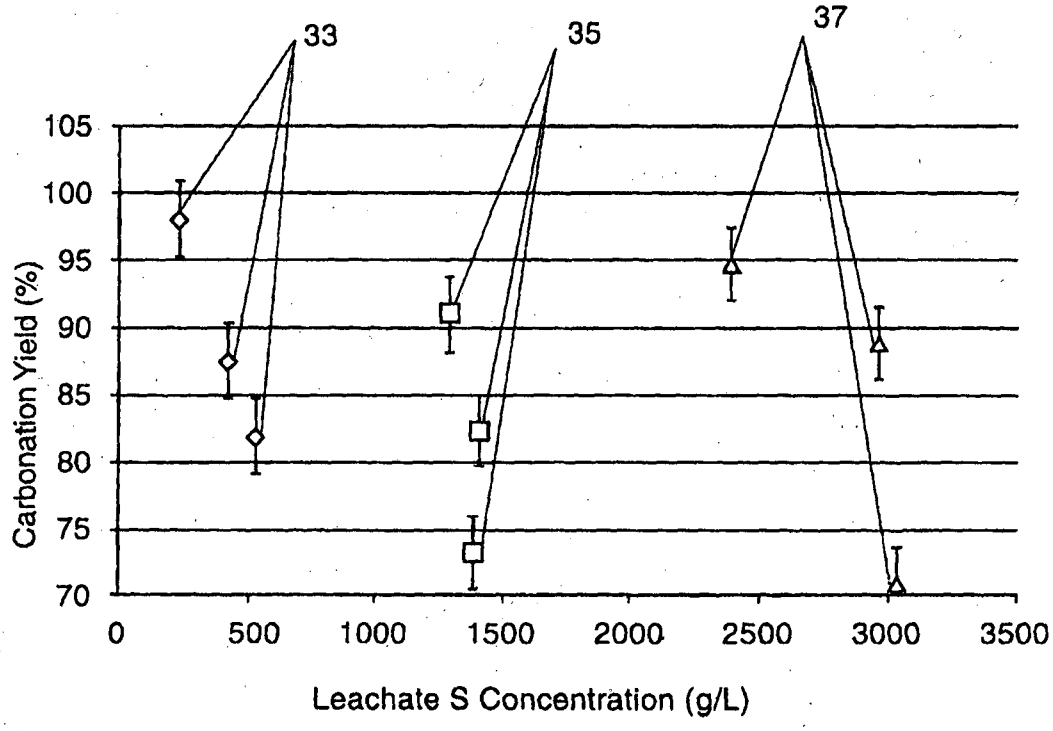


Figure 10

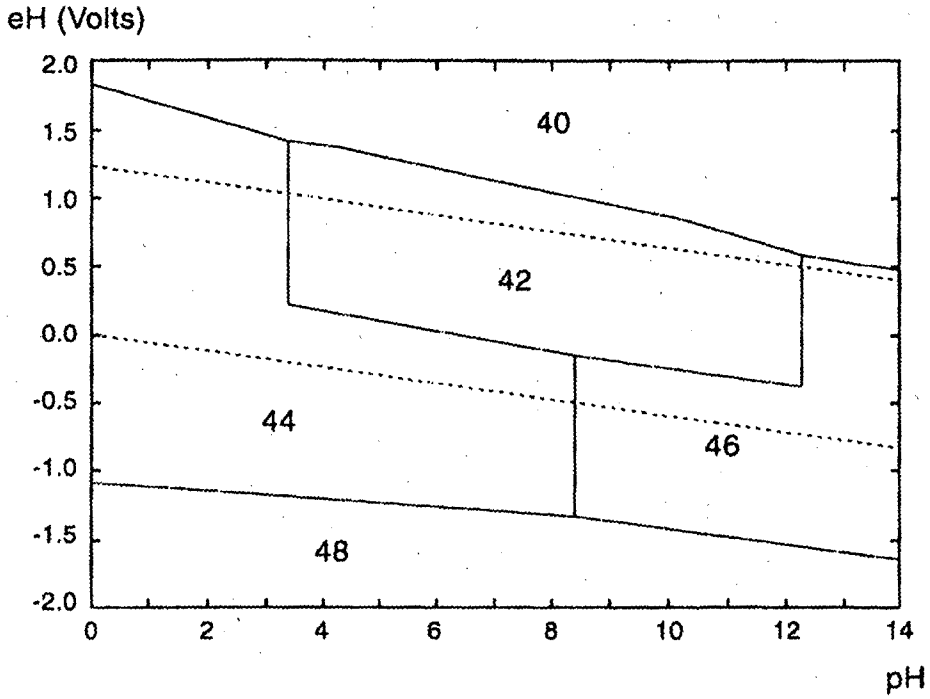


Figure 11(a)

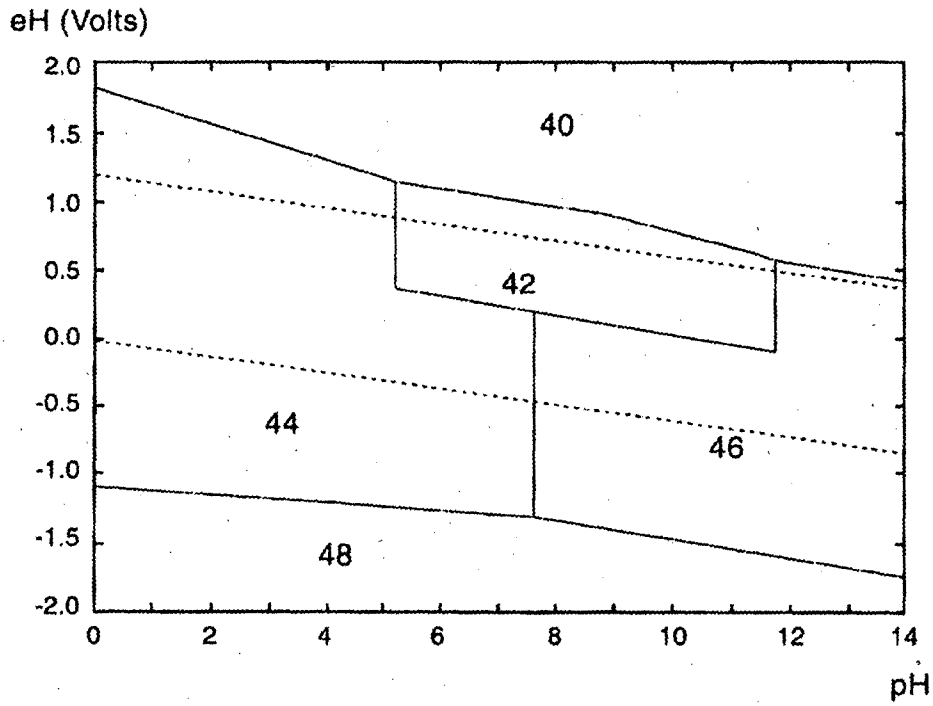


Figure 11(b)

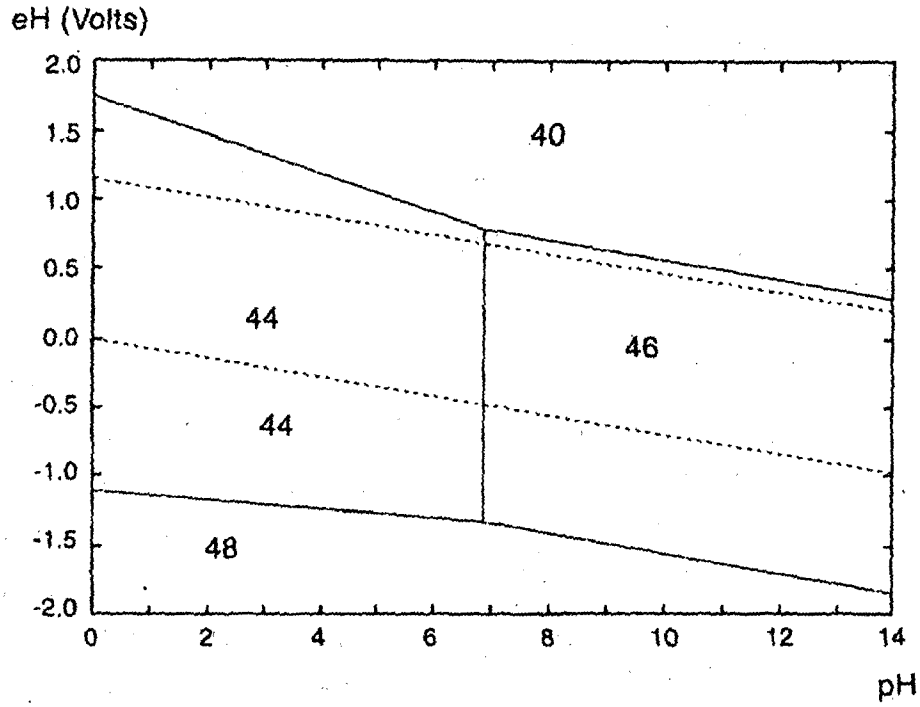


Figure 11(c)

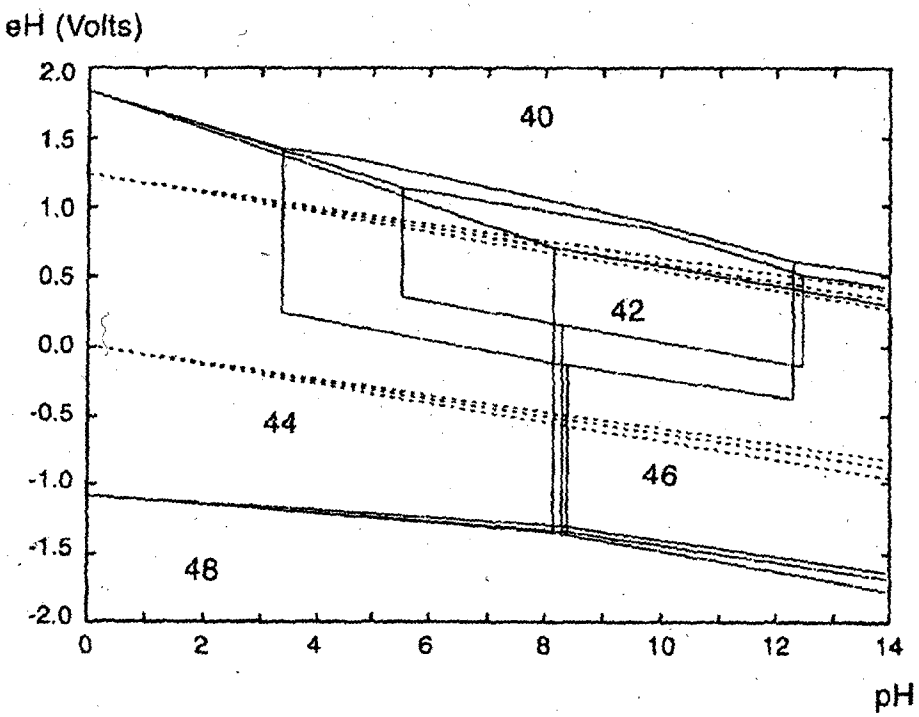


Figure 11(d)

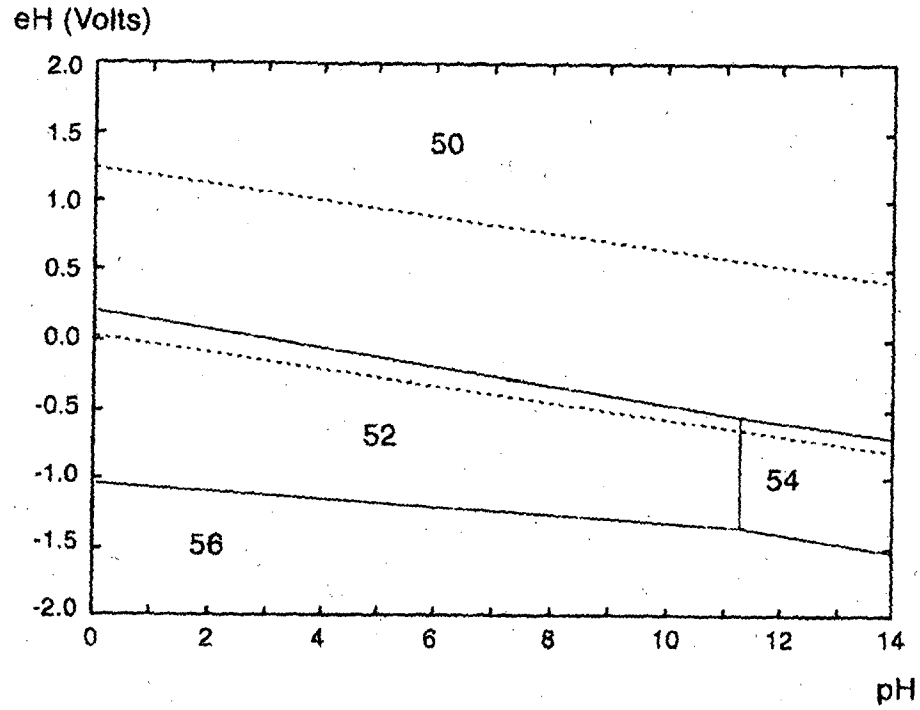


Figure 12(a)

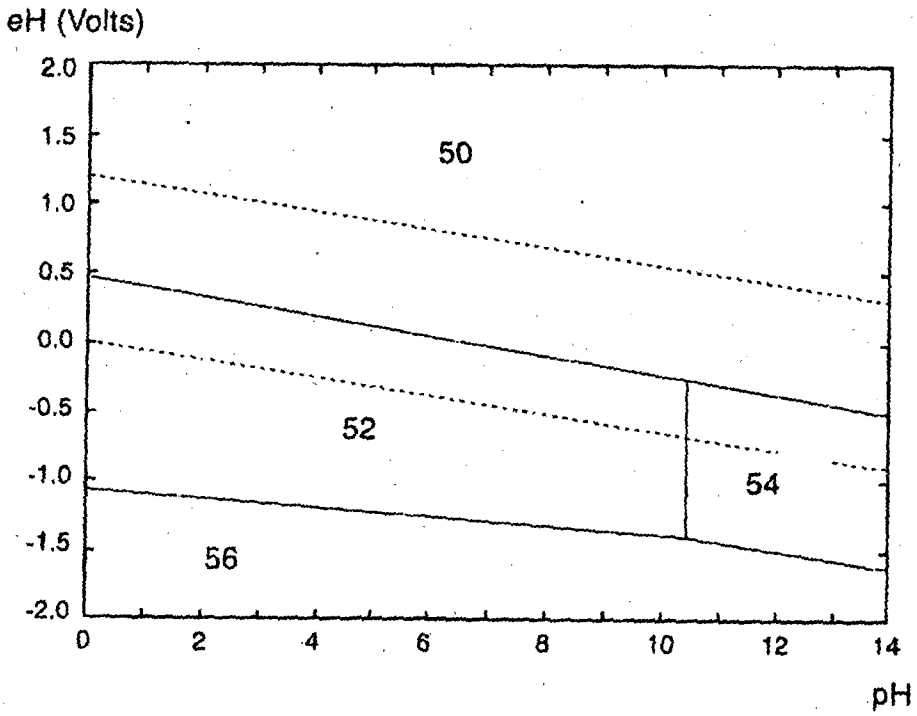


Figure 12(b)

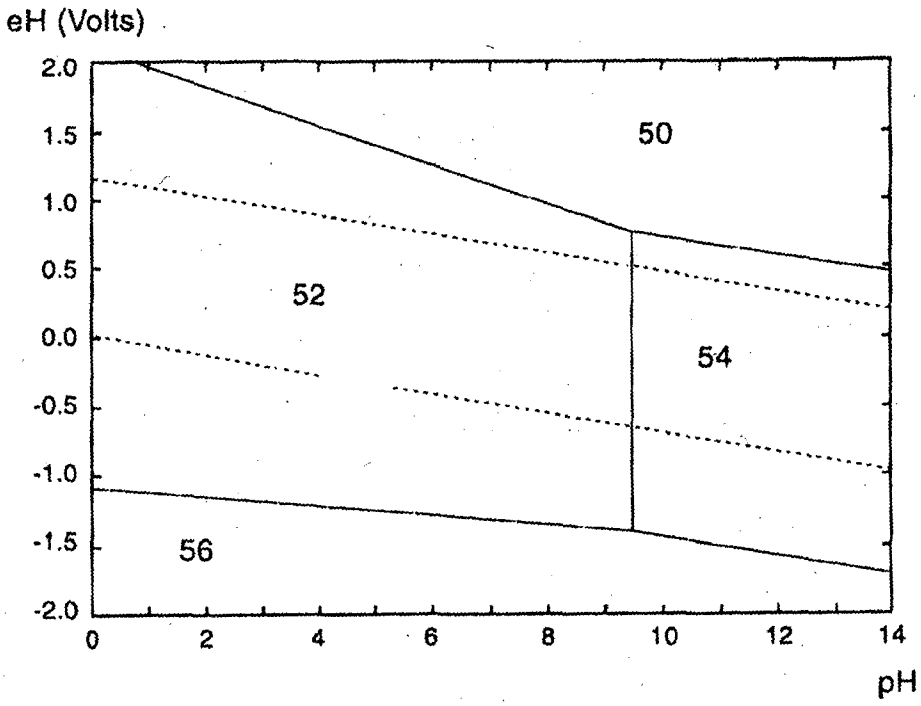


Figure 12(c)

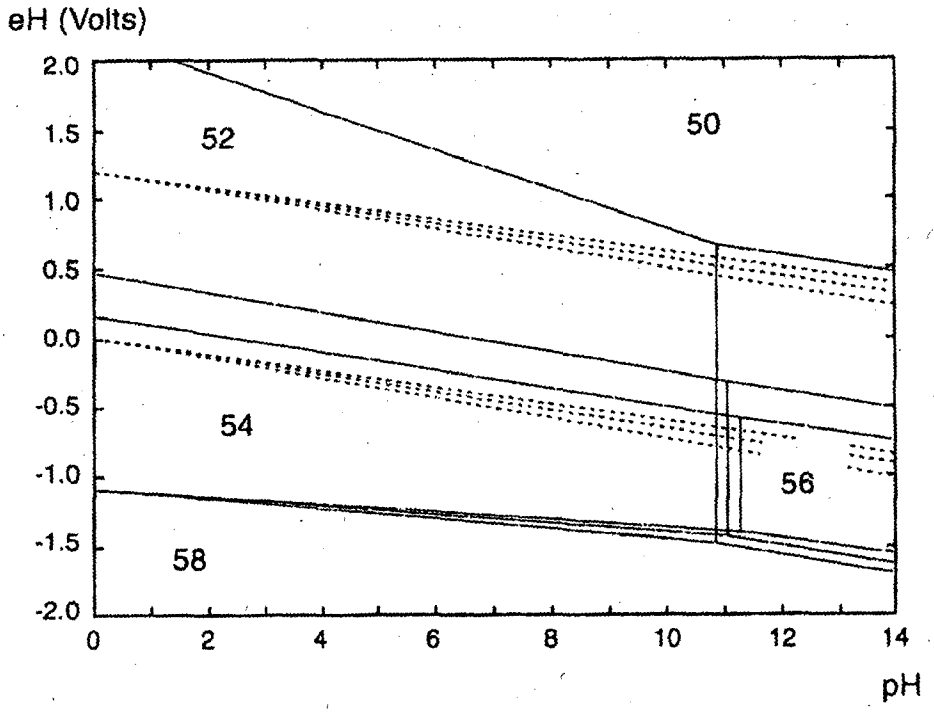


Figure 12(d)

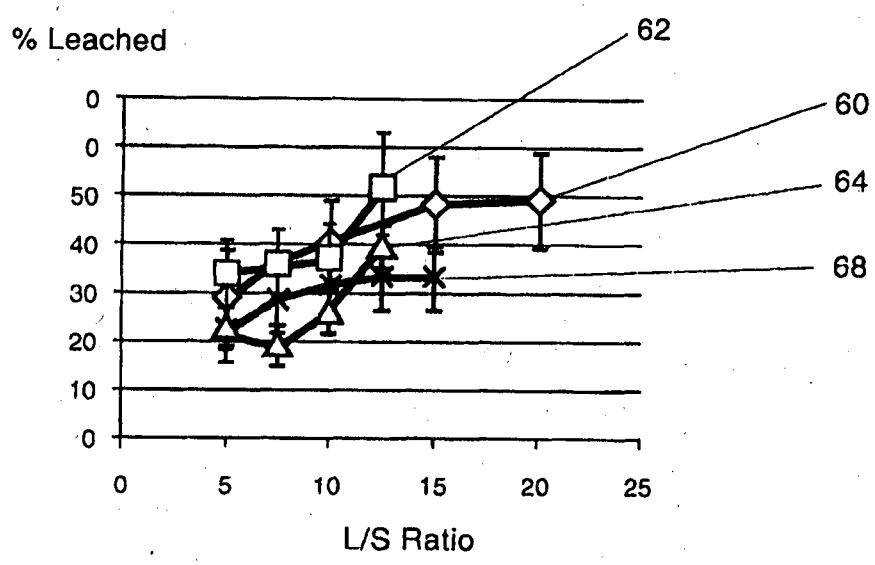


Figure 13(a)

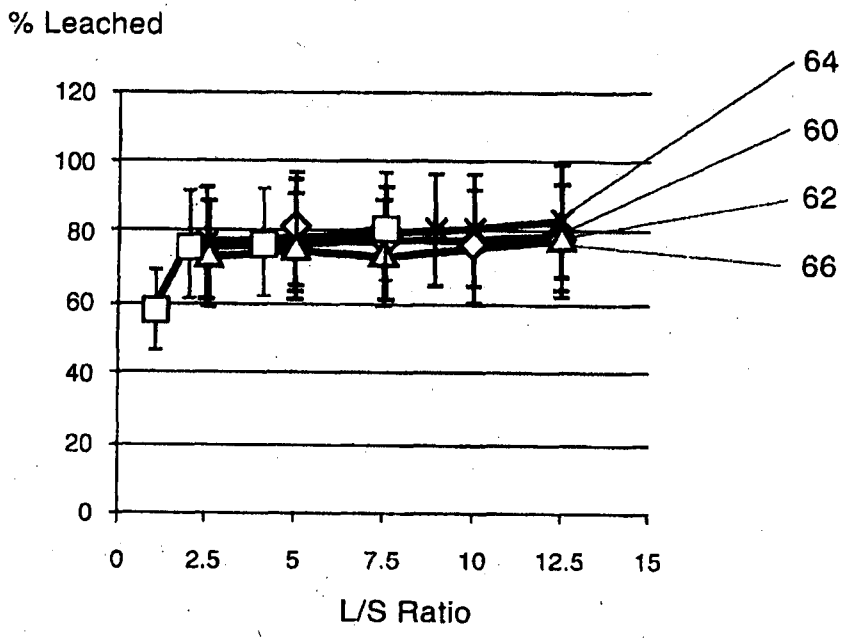


Figure 13(b)

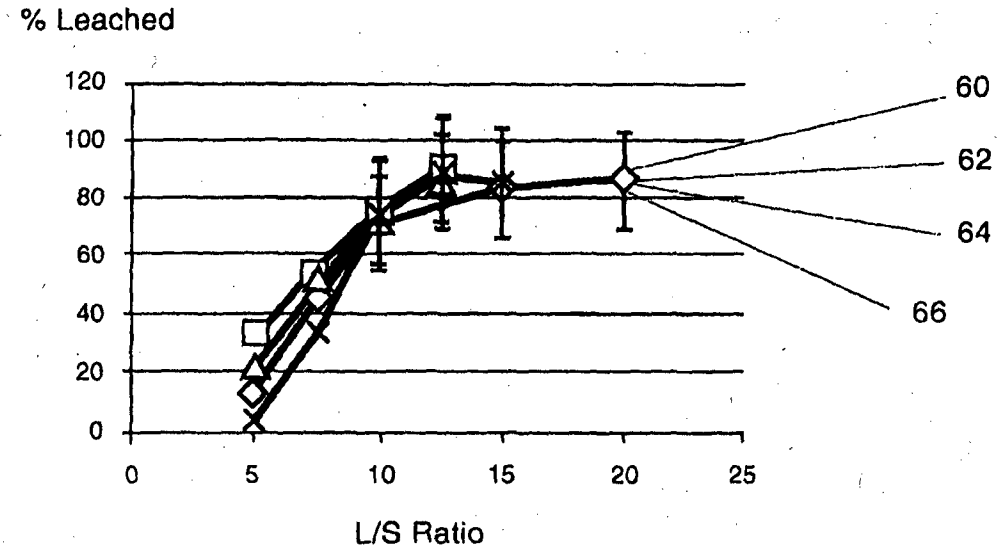


Figure 14(a)

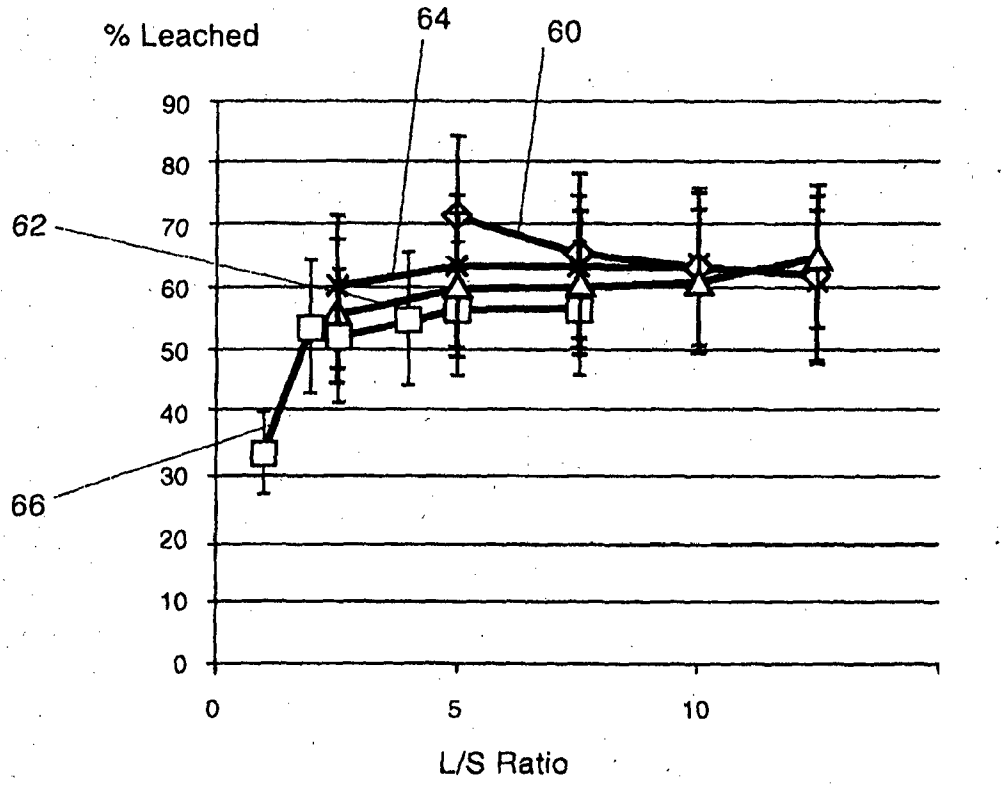


Figure 14(b)

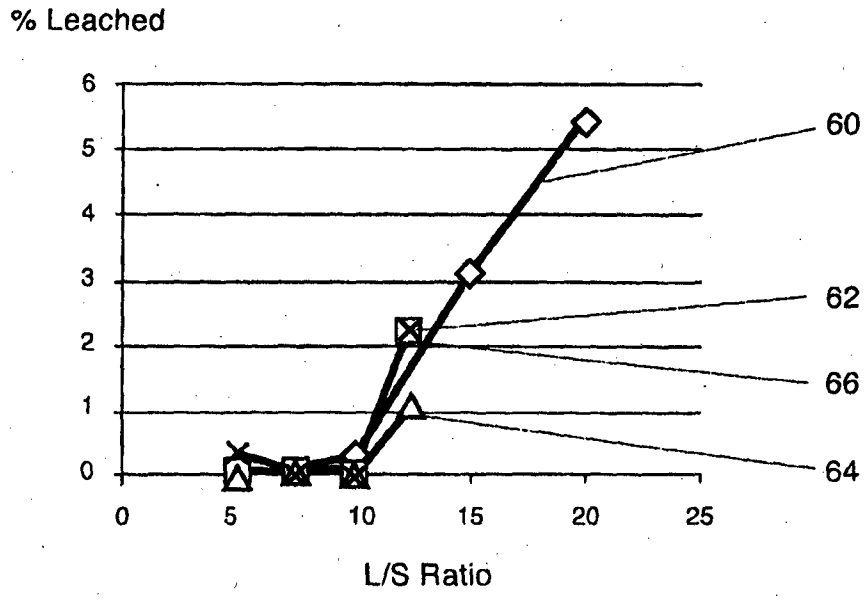


Figure 15(a)

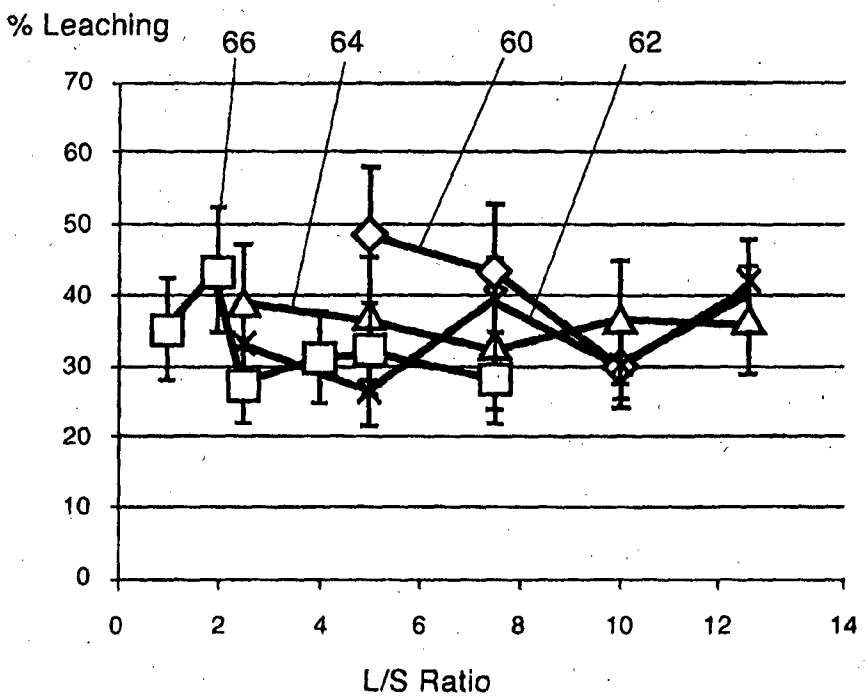


Figure 15(b)

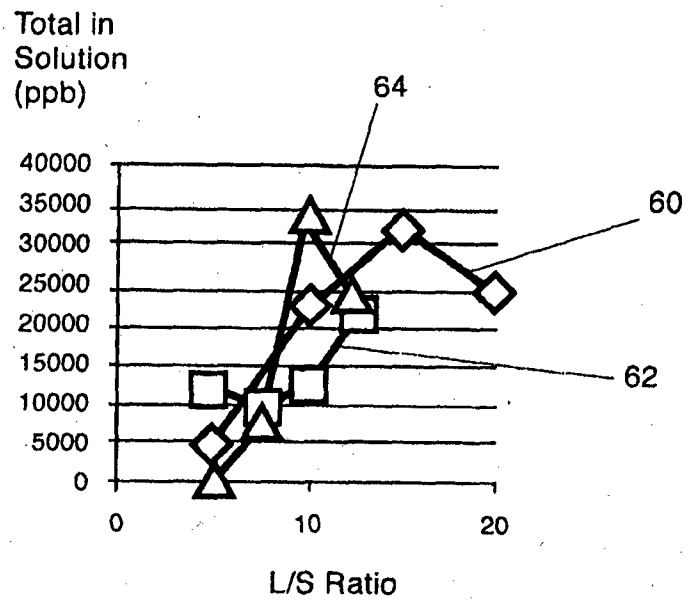


Figure 16(a)

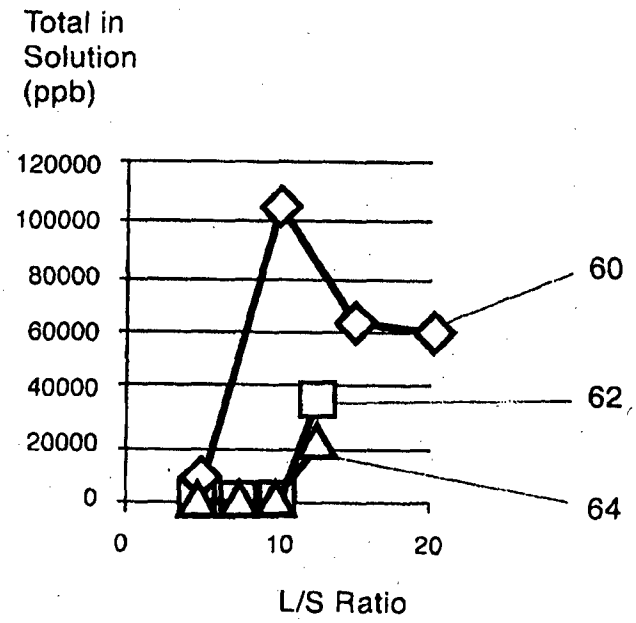


Figure 16(b)

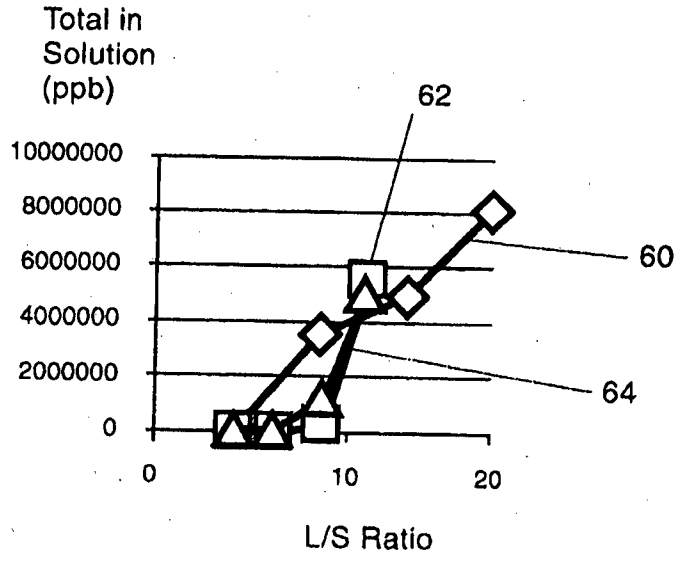


Figure 16(c)

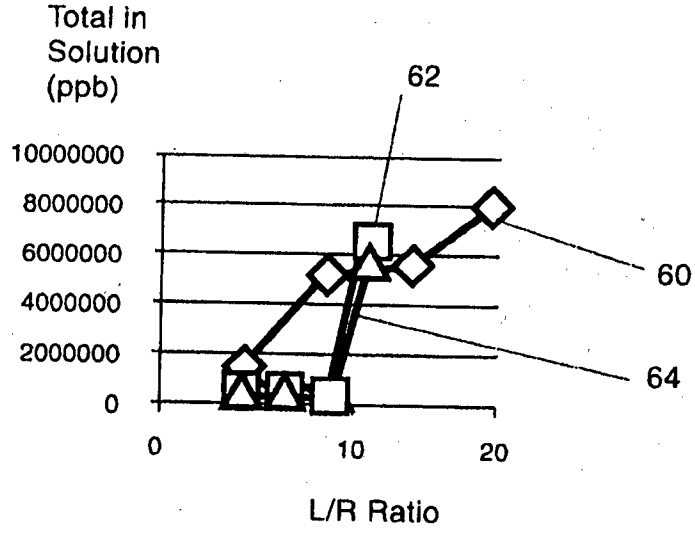


Figure 16(d)

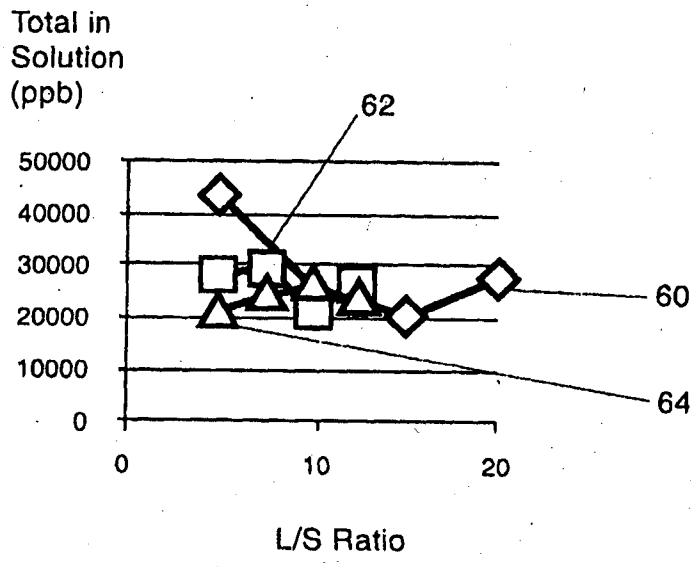


Figure 16(e)

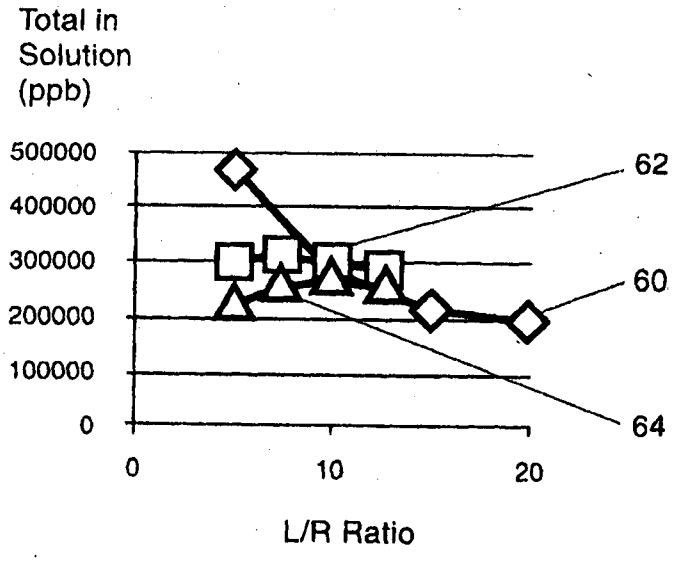


Figure 16(f)

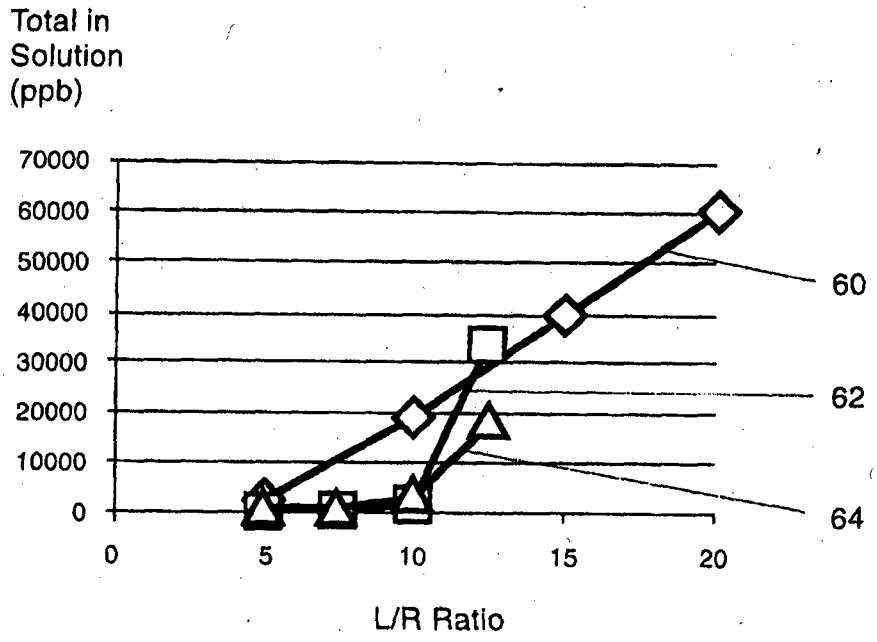

Total in Solution (ppb)
70000
60000
50000
40000
30000
20000
10000
0
0
5
10
15
20
L/R Ratio
60
62
64

Figure 16(g)

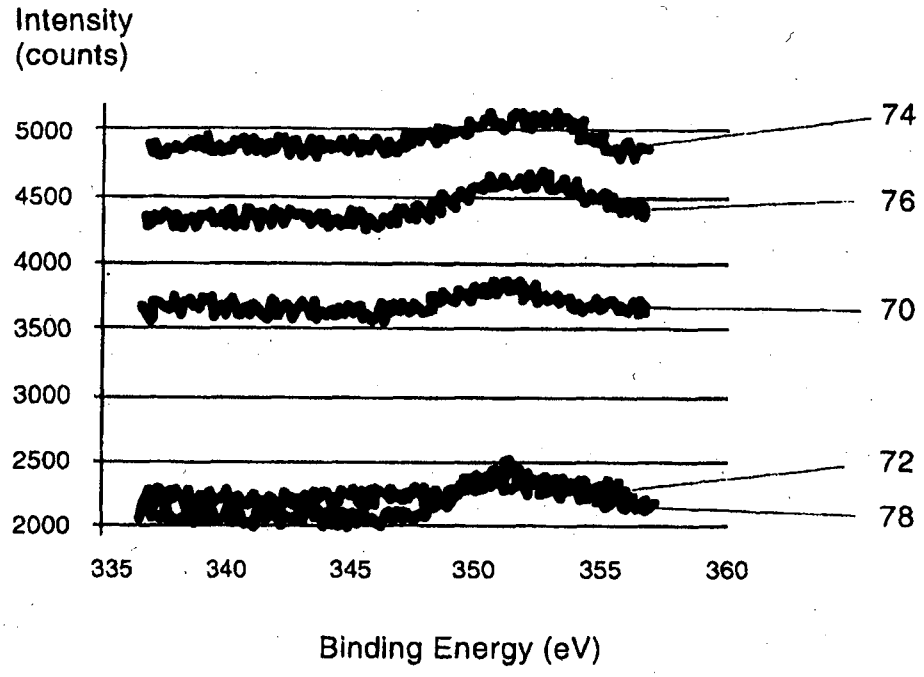
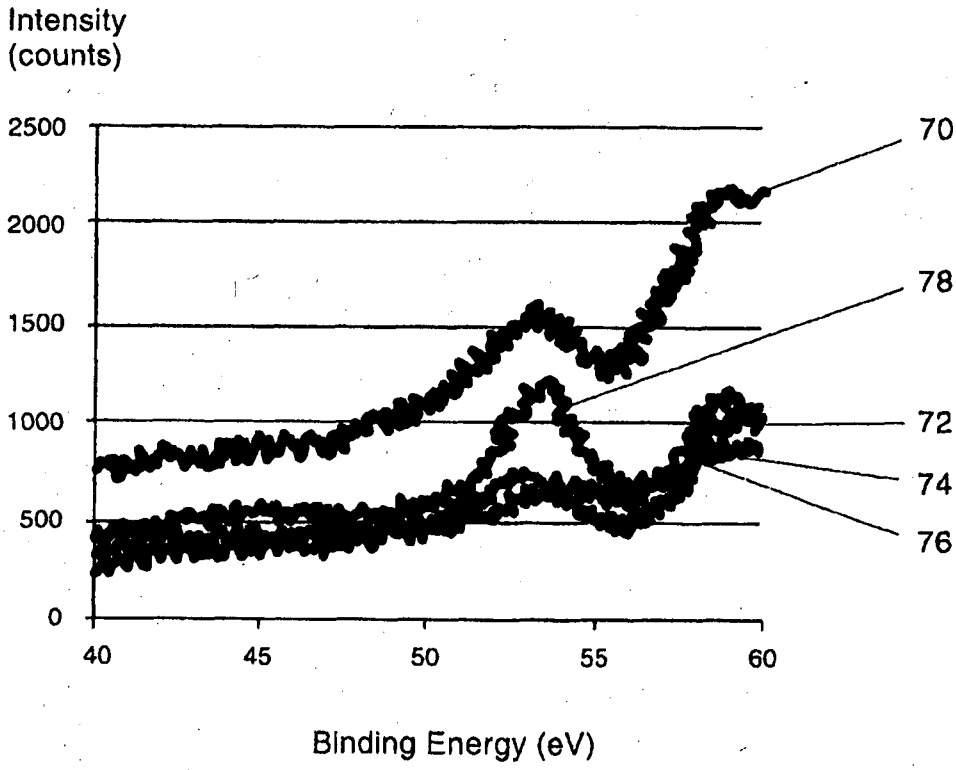


Figure 17(a)



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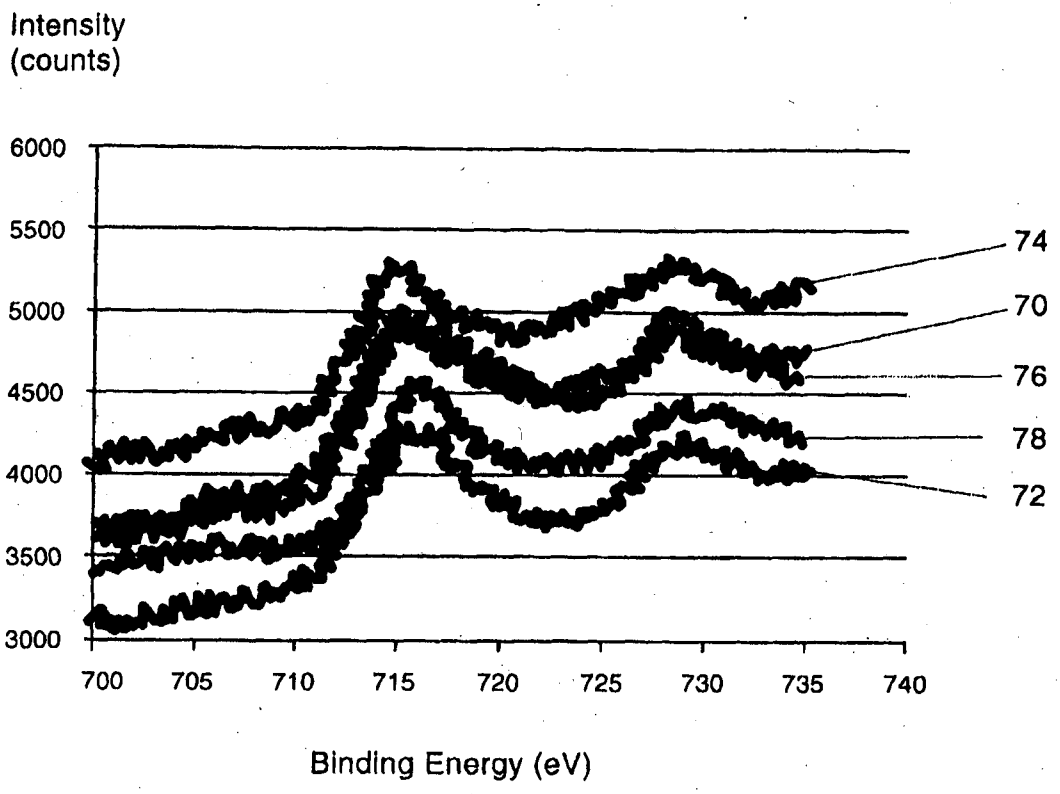

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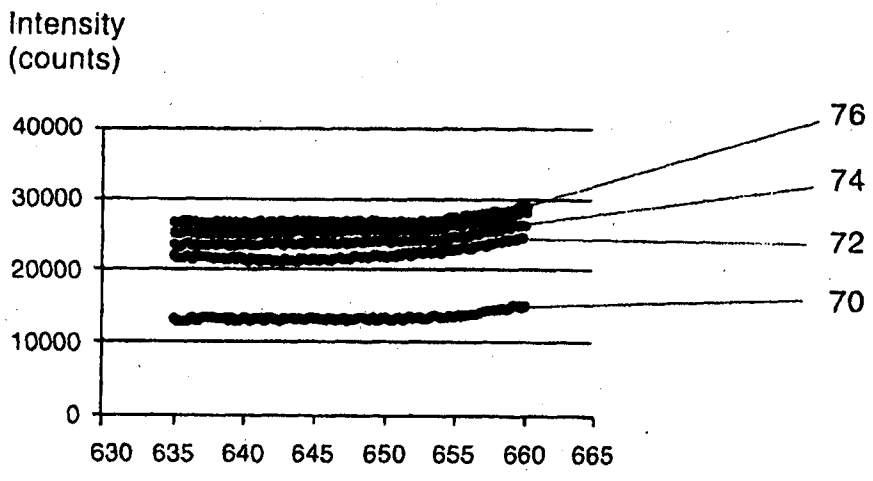

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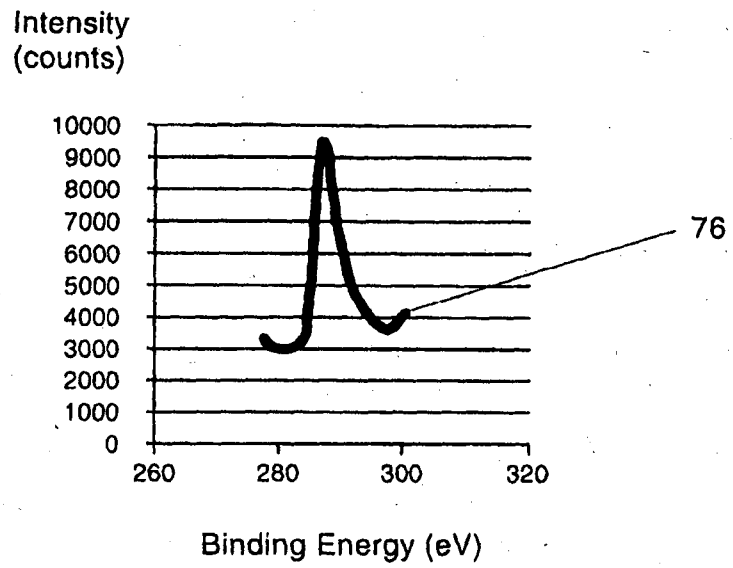

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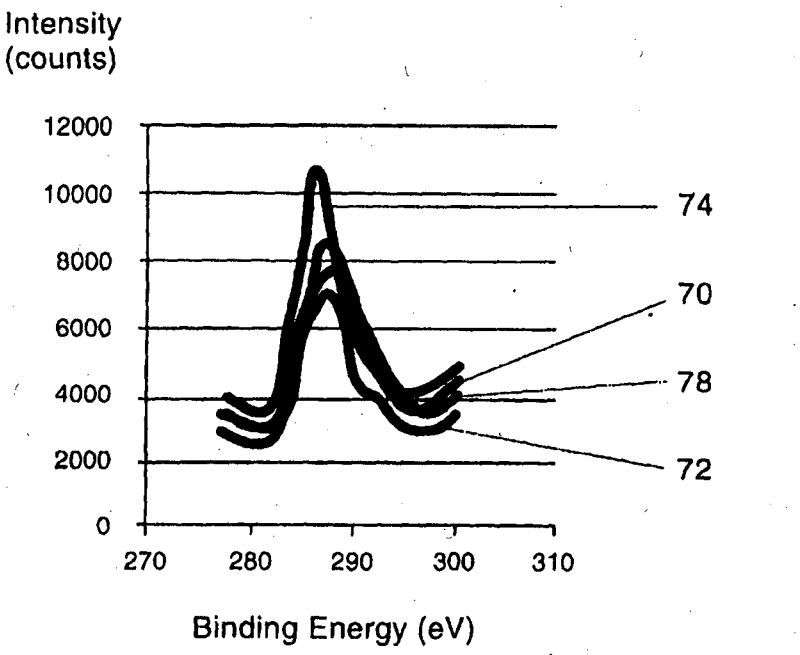

Figure 17(f)

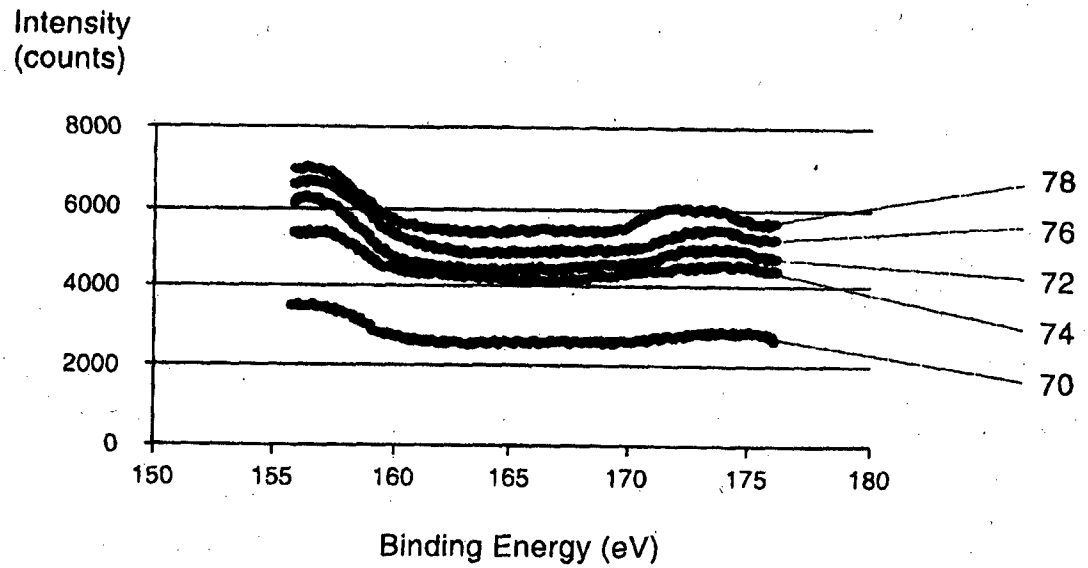
Intensity
(counts)
8000
6000
4000
2000
0
150
155
160
165
170
175
180
78
76
72
74
70
Binding Energy (eV)

Figure 17(g)

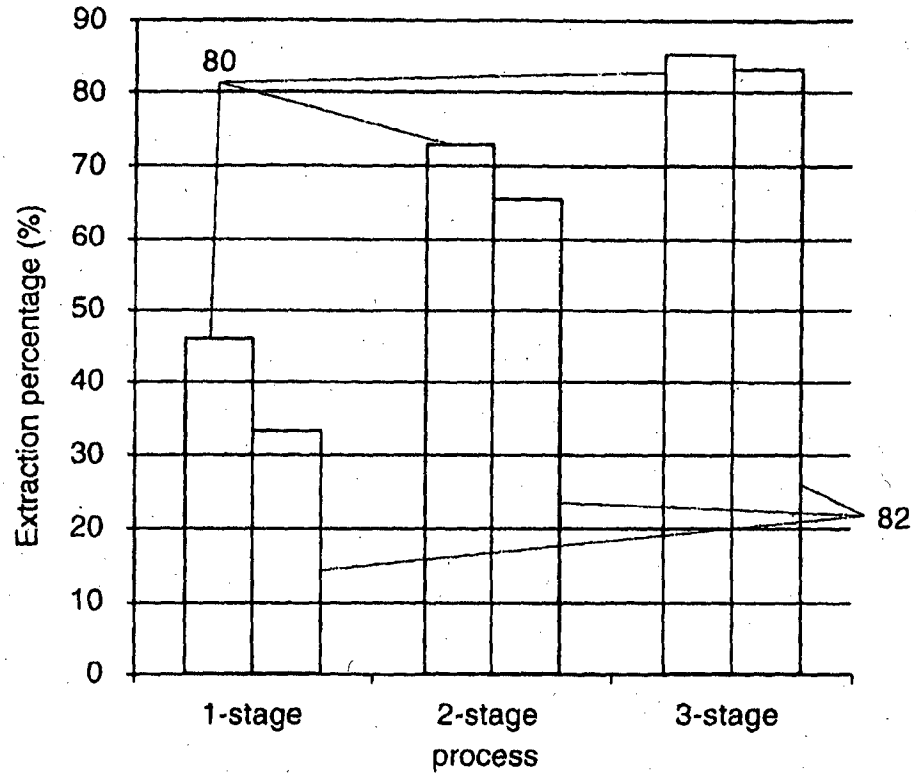

Figure 18

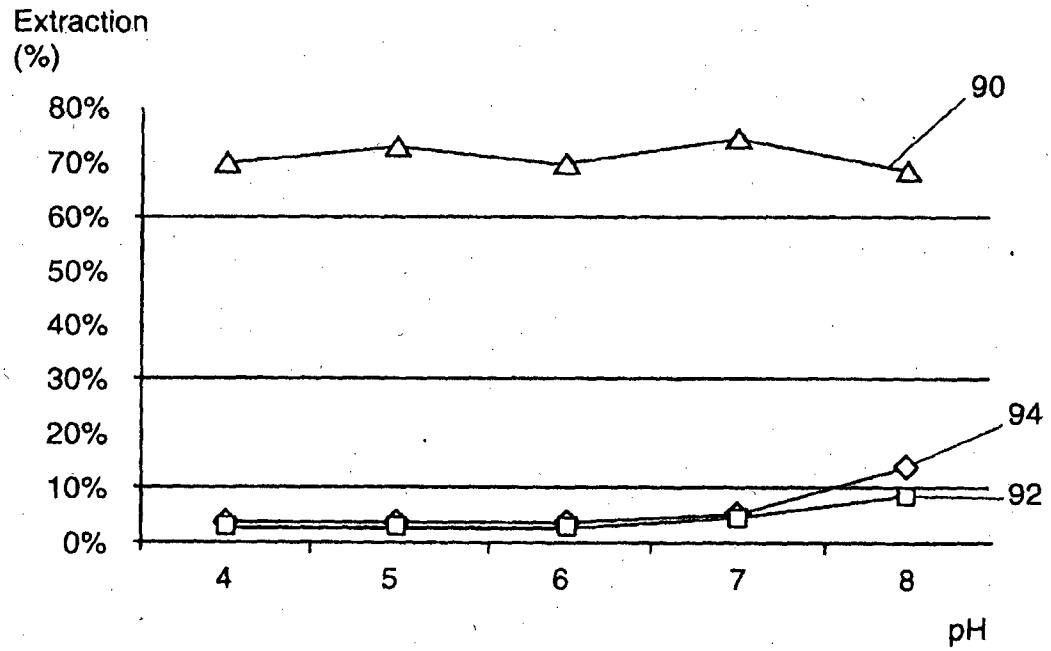

Figure 19

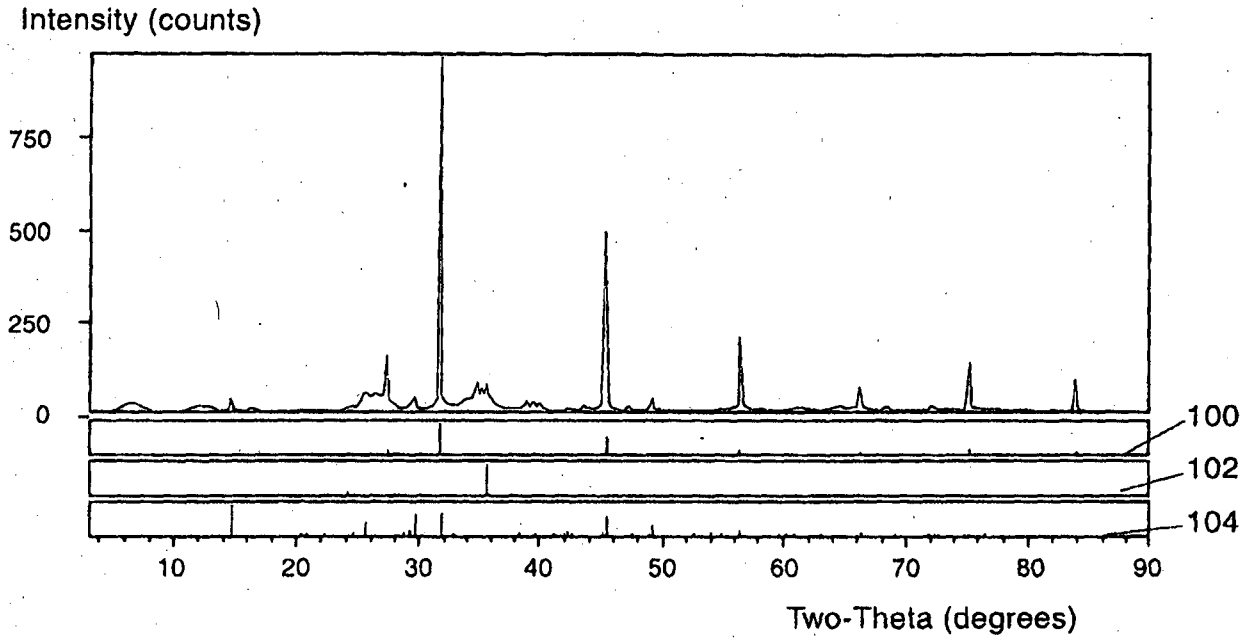

Figure 20

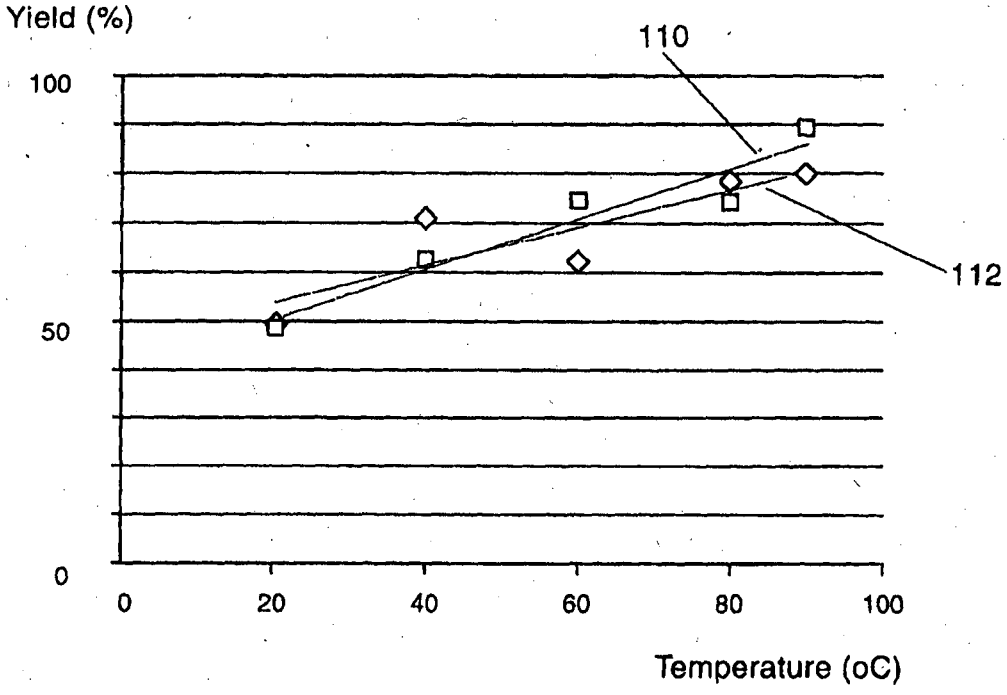

Figure 21

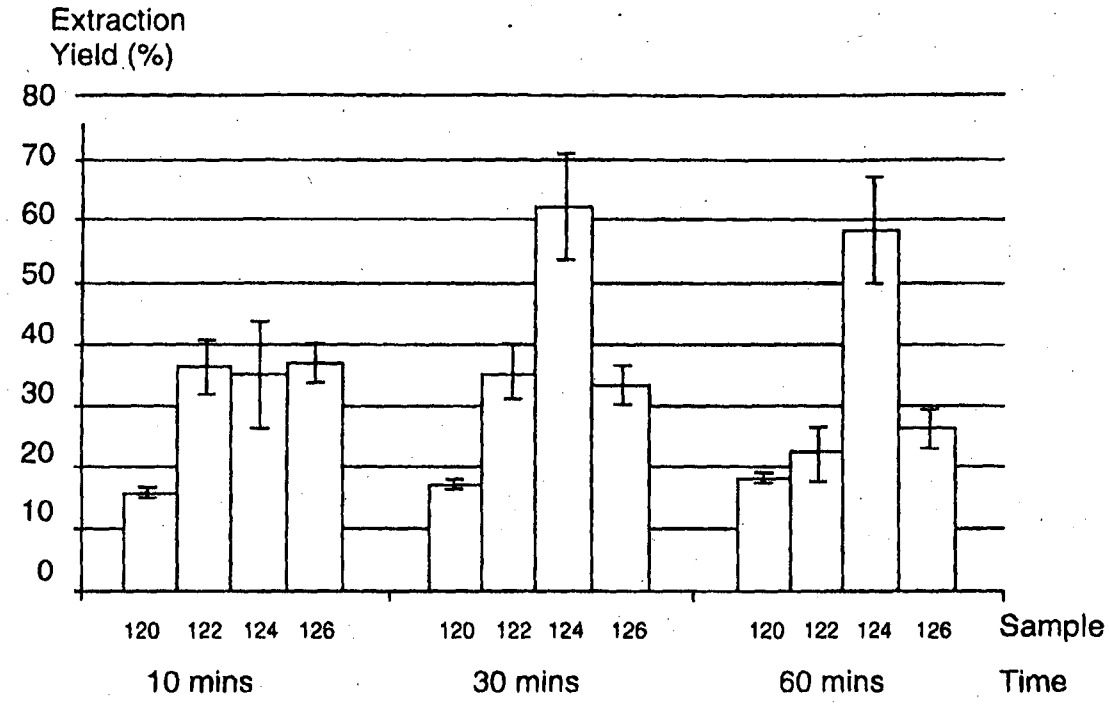

Figure 22(a)

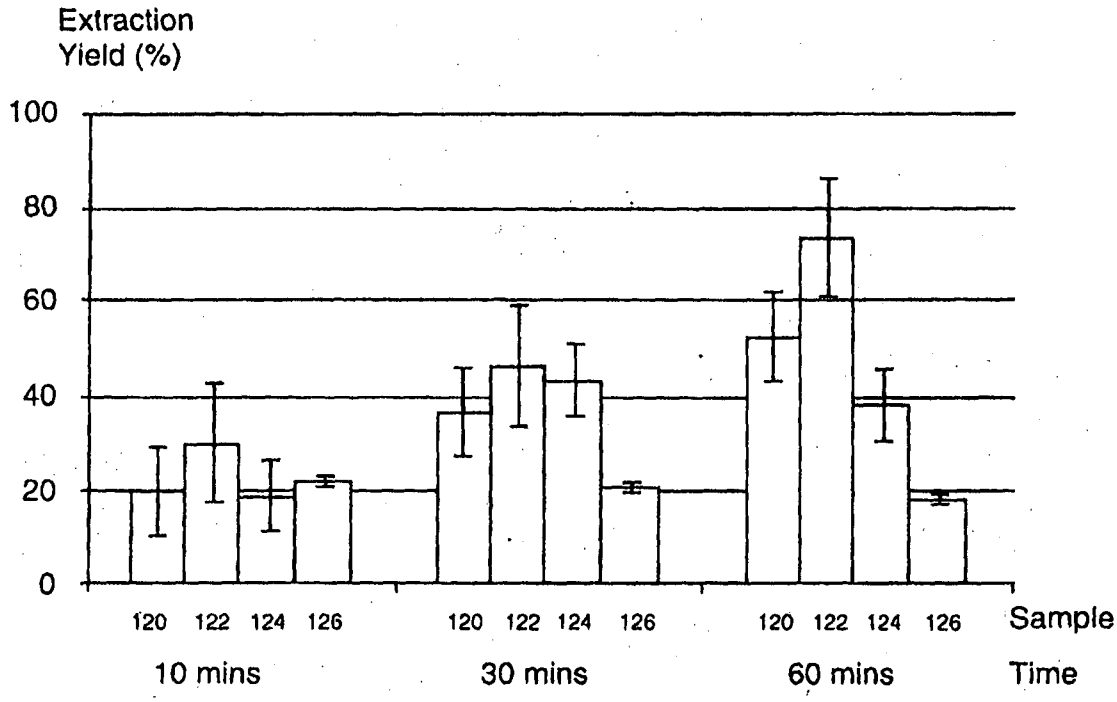

Figure 22(b)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2013/000716

A. CLASSIFICATION OF SUBJECT MATTER

C22B 3/04 (2006.01) B01D 53/78 (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)

WPI, EPODOC: IPC's /IC/CC (B01D/LOW, C22B3/LOW, C22B26/22/LOW, B09B3/LOW, B03B9/04/LOW, F23J15/LOW, Y02C10/LOW, Y02E20/32/LOW, Y02E20/34/LOW, B01D2257/504) & KEYWORDS (LEACH, CARBONATE, PRECIPITATION, FILTRATION AND SIMILAR TERMS). WPI, EPODOC: GENERAL KEYWORD SEARCH USING KEYWORDS (FLY ASH, COAL, COMBUSTION, ASH, LEACH, CARBONATE, PRECIPITATION AND SIMILAR TERMS).

GOOGLE PATENTS, ESPACENET, PATENT LENS: KEYWORDS (LEACH, CARBONATE, FILTRATION, PRECIPITATION, FLY ASH, MAGNESIUM AND SIMILAR TERMS).

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

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

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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
12 September 2013	12 September 2013

Name and mailing address of the ISA/AU

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Authorised officer

Khalid Shamim
AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No. 0262832560

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2013/000716**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ES 2065288 A1 (ESPAN CARBUROS METAL) 01 February 1995 English Abstract obtained from Espacenet; English Translation of full document obtained from Google Translation tool	1, 2, 4-7, 13, 14
A	English Abstract obtained from Espacenet; English Translation of full document obtained from Google Translation tool	3, 8-12

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2013/000716**

This Annex lists known 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/s Cited in Search Report		Patent Family Member/s	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
ES 2065288 A1	01 Feb 1995	ES 2065288 B1	01 Mar 1996

End of Annex

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