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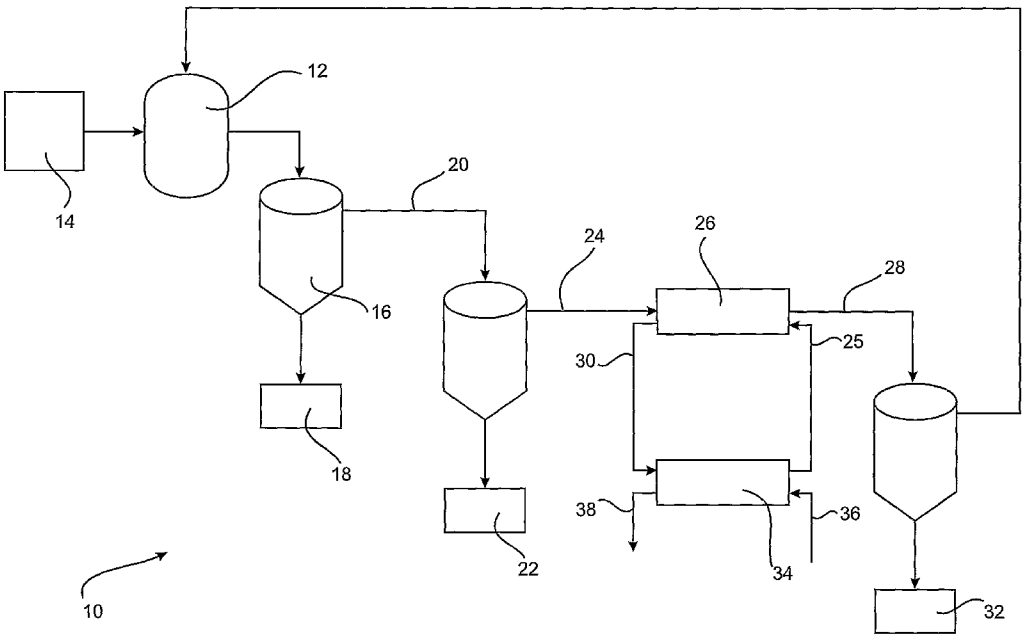
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(54) **Title:** METHOD FOR CONTROLLING THE PRECIPITATION OF ALUMINA



(57) **Abstract:** A method for controlling the precipitation of alumina from Bayer process solutions, the method comprising the steps of: contacting the Bayer process solution with a substantially water- immiscible solution comprising an extractant; extracting at least a portion of the metal cations present in the Bayer process solution into the substantially water-immiscible solution; thereby reducing the concentration of hydroxide ions in the Bayer process solution.

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Method for controlling the precipitation of alumina

Field of the Invention

The present invention relates to a method for controlling the precipitation of alumina from a Bayer process solution.

Background Art

The Bayer process is widely used for the production of alumina from alumina-containing ores such as bauxite. The process involves contacting alumina-containing ores with recycled caustic aluminate solutions at elevated temperatures in a process commonly referred to as digestion. Solids are removed from the resulting slurry and the solution cooled to induce a state of supersaturation.

Alumina is added to the solution as seed to induce precipitation of further aluminium hydroxide therefrom. The precipitated alumina is separated from the caustic aluminate solution (known as spent liquor), with a portion of alumina being recycled to be used as seed and the remainder recovered as product. The remaining caustic aluminate solution is recycled for further digestion of alumina-containing ore.

The precipitation reaction can be generally represented by the following chemical equation with reference to the precipitation of aluminium hydroxide. A similar equation may be prepared for the precipitation of aluminium oxyhydroxide:

$$Al(OH)_4^-(aq) + Na^+(aq) \longrightarrow Al(OH)_3(s) + OH^-(aq) + Na^+(aq)$$

As the precipitation reaction proceeds, the A/TC ratio of the liquor falls from about 0.7 to about 0.4 (where A represents the alumina concentration, expressed as gL^{-1} of Al_2O_3, and TC represents total caustic concentration, expressed as gL^{-1} of sodium carbonate). At the lower value of A/TC, the rate of precipitation slows

substantially due to a decrease in the level of supersaturation, and an increase in the level of "free caustic" in the liquor, as the system approaches equilibrium.

It is known that the TC and TA (where TA represents total alkali concentration, expressed as gL^{-1} of sodium carbonate) of Bayer process solutions affects the solubility of boehmite and gibbsite in those solutions in a number of ways.

Generally, more than half of the alumina stays dissolved in solution, to be recycled through the digestion circuit of the plant. In principle, if some of the hydroxide formed during precipitation could be removed, the A/TC ratio of the liquor would increase and the equilibrium of the above reaction would be shifted to the right favouring more precipitation of alumina. Further, it is believed that supersaturation could also be induced, and controlled, by reducing the level of caustic in Bayer liquor with the benefit of achieving an increase in yield beyond that which is attainable under current practices.

Liquor carbonation is a technique used in the alumina industry to convert hydroxide to carbonate, and has been used to increase the precipitation yield of alumina. However, apart from producing alumina of inferior quality compared to current practices, liquor carbonation necessitates the excessive purchase cost of lime which is required to regenerate caustic from sodium carbonate. Further, the recausticisation step is inefficient and does not result in complete regeneration of the caustic.

Based on alumina solubility alone, the extraction of sodium ions in conjunction with the neutralisation of hydroxide should produce a greater increase in precipitation yield than hydroxide neutralisation by carbonation. This is because the former leads to a reduction in both TC and TA whereas the latter leads to a reduction in TC but TA remains constant (where TC and TA represent the total caustic concentration and the total alkali concentration respectively, both expressed as gL^{-1} sodium carbonate). For a given value of TC, alumina is more soluble in solutions of higher TA.

US6322702 teaches the use of solvent extraction technology to extract sodium ions from alkaline waste solutions from nuclear processes. The hydroxide extraction technology is based on cation exchange principles and involves the exchange of a proton from an acidic lipophilic reagent (HA) dissolved in a non-aqueous solvent, for an aqueous sodium ion at high pH in accordance with the following equation:

$$Na^+ (aq) + OH^- (aq) + HA (org) \rightleftharpoons H_2O + NaA (org)$$

US6322702 indicates that the alumina industry could use the invention disclosed therein to recover NaOH from waste streams. They assert that a secondary advantage of the invention is that removal of NaOH will reduce the pH of the stream below 12.5 which can then more easily be disposed of. When read in this context, US6322702 clearly is referring to the disposal of Bayer processing waste streams, such as "red mud", which is the highly alkaline bauxite residue separated after alumina extraction with caustic. The teachings of the patent are not directed at Bayer liquor, which is continuously recycled within the plant between the digestion and precipitation circuits. Furthermore, the document does not teach or infer use of the invention to drive the precipitation reaction to increase alumina precipitation.

The preceding discussion of the background to the invention is intended to facilitate an understanding of the present invention. However, it should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was part of the common general knowledge in Australia, or anywhere else, as at the priority date of the application.

Disclosure of the Invention

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. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in the specification, individually or

collectively and any and all combinations or any two or more of the steps or features.

The present invention is not to be limited in scope by the specific embodiments described herein, which are intended for the purpose of exemplification only. Functionally equivalent products, compositions and methods are clearly within the scope of the invention as described herein.

The entire disclosures of all publications (including patents, patent applications, journal articles, laboratory manuals, books, or other documents) cited herein are hereby incorporated by reference.

In accordance with the present invention, there is provided a method for controlling the precipitation of alumina from a Bayer process solution, the method comprising the steps of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant;

extracting a metal cation present in the Bayer process solution into the substantially water-immiscible solution;

thereby reducing the concentration of hydroxide ions in the Bayer process solution.

As used herein the term "alumina" shall be taken to include, without limitation, any form of aluminium hydroxide, aluminium oxyhydroxide or aluminium oxide.

It will be appreciated that the extraction of the metal cation from the Bayer process solution into the substantially water-immiscible solution will encompass the extraction of metal cations from the Bayer process solution into the substantially water-immiscible solution.

Advantageously, the extraction of a metal cation into the substantially water-immiscible solution leads to a concomitant transfer of a cation from the

substantially water-immiscible solution to the Bayer process solution. The cation neutralises hydroxide ions present thereby enhancing alumina precipitation.

The present invention offers distinct advantages over methods employing carbonation to reduce hydroxide concentrations in Bayer process solutions, as carbonation reduces TC without affecting TA, but the present invention reduces both the TC and TA of the Bayer process solution.

Preferably, the method comprises the further step of:

precipitation of alumina in the Bayer process solution.

Alumina is more soluble in alkaline solutions than in water and advantageously, the reduction of hydroxide concentration in the Bayer process solution can increase precipitation of alumina.

Advantageously, the method of the present invention may be utilised to control the form of precipitated alumina and influence the formation of forms such as boehmite, gibbsite, bayerite, doyleite and nordstrandite. It will be appreciated that the alumina may be a mixture of any of the preceding forms.

Preferably, the method comprises the further step of:

seeding the Bayer process solution with alumina.

In one form of the invention, the step of:

seeding the Bayer process solution with alumina

is conducted prior to the step of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant.

In a second form of the invention, the step of:

seeding the Bayer process solution with alumina

is conducted after the step of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant.

It will be appreciated that the optimal seeding rate will depend on many factors, including the seed and liquor properties and the design of the precipitation circuit, and may be greater than 50 gL^{-1} and preferably, in the range of 50 to 1300 gL^{-1}.

Advantageously, the present invention can negate the need to reduce the temperature of Bayer process solutions to encourage supersaturation. It is known that precipitation rates decrease with temperature. In a gibbsite precipitation circuit, precipitation commences at about 90 °C and ends at about 60 °C at the completion of the precipitation phase. Without being limited by theory, it is believed that the method of the present invention may permit precipitation of alumina at temperatures as high as the boiling point of the liquor at that pressure.

The present invention may be utilised to increase precipitation yields beyond current limits without initially increasing TC in digestion. It may provide means of inducing supersaturation without appreciable liquor cooling.

Without being limited by theory, it is believed that a sodium/aluminate ion pair exists on or near the surface of precipitated alumina and hinders further deposition of alumina onto the surface. Advantageously, removing sodium from the Bayer process solution is believed to increase alumina precipitation.

Importantly, the present invention does not advocate a measurable reduction in solution pH as is specified in US6322702. Bayer liquor pH is above measurable limits (>14) and it has been discovered that a significant increase in precipitation yield can be obtained by instigating a decrease in caustic concentration by solvent extraction, whereby liquor pH is still kept well above a value of 14.

Preferably, the extractant is provided in the form of a weak acid.

Where the extractant is provided in the form of a weak acid, the extraction of the metal ion into the substantially water-immiscible solution will be accompanied by the transfer of a proton from the substantially water-immiscible solution into the Bayer process solution.

Preferably, the metal cation is provided in the form of a sodium ion.

Preferably, the weak acid extractant comprises at least one polar group with an ionisable proton with a pKa of between about 9 and about 13.

The extractant is preferably a straight chain, branched chain or cyclic hydrocarbon, a halogenated hydrocarbon, an aliphatic or aromatic ether or alcohol with more than 6 carbon atoms. Preferably, the extractant comprises an alcohol or phenol functional group. Suitable extractants include 1H,1H-perfluorononanol, 1H,1H,9H-hexadecafluorononanol, 1,1,1-trifluoro-3-(4-*tert*-octylphenoxy)-2-propanol, 1,1,1-trifluoro-2-(*p*-tolyl)*iso*propanol, 1-(*p*-tolyl)-2,2,2-trifluoroethanol, hexafluoro-2-(*p*-tolyl)isopropanol, 2-(methyl)-2-(dodecyl)tetradecanoic acid, 3-(perfluorohexyl)propenol and 1-(1,1,2,2-tetrafluoroethoxy)-3-(4-*tert*-octylphenoxy)-2-propanol, *tert*-octylphenyl, *para*-nonylphenol, *para*-*tert*-butylphenol, *para*-*tert*-amylphenol, *para*-heptylphenol, *para*-octylphenol, *para*-(alpha,alpha-dimethylbenzyl)phenol (4-cumylphenol), 2,3,6-trimethylphenol, 2,4-di-*tert*-butylphenol, 3,5-di-*tert*-butylphenol, 2,6-di-*tert*-butylphenol, 2,4-di-*tert*-pentylphenol (2,4-di-*tert*-amylphenol), 4-sec-butyl-2,6-di-*tert*-butylphenol, 2,4,6-tri-*tert*-butylphenol, 2,4-bis(alpha,alpha-dimethylbenzyl)phenol (2,4-dicumylphenol) and other alkylated phenols or mixtures thereof.

It should be appreciated the substantially water-immiscible solution may form the extractant.

Preferably, the acidic form of the extractant is substantially insoluble in water.

Preferably, the deprotonated form of the extractant is substantially insoluble in water.

It should be appreciated that partitioning of the extractant in the Bayer process solution should be minimal.

It should be appreciated that the extractant concentration will depend on a number of factors including the intended amount of induced supersaturation which in turn will be influenced by the temperature at which precipitation will be initiated.

It should be appreciated that the degree of deprotonation in the extraction step will depend on the acidity of the ionisable proton (as well as the pH and salt content of the Bayer process solution).

Reactions between substances distributed in different phases can be slow because, in a reaction of first order with respect to each of the two components, the rate is maximised when the concentrations of the species in a given phase are maximised. The use of phase transfer catalysts may enhance extractions rates. Suitable phase transfer catalysts may be selected from lipophilic quaternary ammonium or phosphonium salts or organic macrocycles such as crown ethers, calixarenes, calixarene-crown ethers, spherands and cryptands.

Specific complexing ligands may be added to the organic mixtures, to either synergistically enhance sodium ion extraction, and/or to additionally extract impurities from Bayer liquor and enhance precipitation in a secondary manner.

The step of contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant may be performed in a process side stream.

In one form of the invention, where the Bayer process includes the steps:

digestion of bauxite with caustic solution;

liquid-solid separation to provide a residue and a liquor; and

precipitation of alumina from the liquor; and

the steps of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant; and

extracting at least a portion of the metal cations present in the Bayer process solution into the substantially water-immiscible solution;

are conducted prior to the step of:

precipitation of alumina from the liquor.

In a second form of the invention, where the Bayer process includes the steps:

digestion of bauxite with caustic solution;

liquid-solid separation to provide a residue and a liquor; and

precipitation of alumina from the liquor; and

the steps of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant; and

extracting at least a portion of the metal cations present in the Bayer process solution into the substantially water-immiscible solution;

are conducted after the step of:

precipitation of alumina from the liquor.

In a third form of the invention, where the Bayer process includes the steps:

digestion of bauxite with caustic solution;

liquid-solid separation to provide a residue and a liquor; and

precipitation of alumina from the liquor; and

the steps of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant; and

extracting at least a portion of the metal cations present in the Bayer process solution into the substantially water-immiscible solution;

are conducted during the step of:

precipitation of alumina from the liquor.

Preferably, the substantially water-immiscible solution is an organic liquid, a combination of organic liquids or an ionic liquid.

Preferably, the organic liquid is substantially non-polar.

Preferably, the organic liquid is a high boiling organic liquid with a low vapour pressure at Bayer process temperatures.

Preferably, the organic liquid is alkaline stable.

The organic liquid is preferably a straight chain, branched chain or cyclic hydrocarbon, a halogenated hydrocarbon, an aliphatic or aromatic ether or alcohol with more than 4 carbon atoms. Suitable solvents include benzene, toluene, xylene, stilbene, 1-octanol, 2-octanol, 1-decanol, *iso*-octyl alcohol (such as that commercially available as Exxal 8 from ExxonMobil), iso-nonylalcohol (such as that commercially available as Exxal 9 from ExxonMobil), *iso*-decanol, *iso*-tridecanol, 2-ethyl-1-hexanol, kerosene and other hydrocarbons commercially

available under the names Escaid 100, Escaid 110, Escaid 240, Escaid 300, Isopar L, Isopar M, Solvesso 150 from ExxonMobil) and mixtures thereof.

It should be appreciated that partitioning of the organic liquid and the extractant in the Bayer process solution should be minimal.

Preferably, the organic liquid solvates the extractant in both its acid and sodium salt forms.

It should be appreciated that the volume of substantially water-immiscible solution relative to the volume of the Bayer process solution may vary according to the manner in which both the Bayer process solution and the substantially water-immiscible solution are contacted and the loading of the extractant in the substantially water-immiscible solution.

The present invention permits the precipitation of alumina at higher temperatures than conventional precipitation techniques. In a normal gibbsite precipitation circuit, supersaturation is only created by lowering the temperature to below about 90 °C. It is known to use a series of precipitators where each subsequent precipitator operates at a lower temperature, and where the last tank out of, for example, seven in series is at 60-70 °C. Lowering the temperature simultaneously reduces precipitation kinetics.

Preferably, the step of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant;

comprises agitating the Bayer process solution and the substantially water-immiscible solution by any means known in the art including shaking, stirring, rolling and sparging.

It will be appreciated that the contact time between the Bayer process solution and the organic phase should be sufficient for reaction to occur between the

extractant and the metal cations to form a metal cation-depleted aqueous phase and a proton-depleted organic phase. Said contact time will be influenced by many factors including the pKa of the ionisable proton on the extractant, the pH of the aqueous phase, the volumes of the aqueous and organic phases, the temperature, the concentration of the extractant and sodium ions, the total alkalinity, the total caustic concentration, the extent of agitation and the presence of other species in the liquor.

It should be appreciated that the volumes of the Bayer process solution and the substantially water-immiscible solution need not be the same. It should be appreciated that where the method is performed as a countercurrent flow or continuous processing, volumes of the phases are less critical than with batch methods.

It will be appreciated that the steps of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant;

extracting a metal cation present in the Bayer process solution into the substantially water-immiscible solution;

may be repeated.

Where the steps of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant;

extracting a metal cation present in the Bayer process solution into the substantially water-immiscible solution;

are repeated, the step of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant;

may be performed with different substantially water-immiscible solutions.

Preferably, the method comprises the further step of:

separating the Bayer process solution and the substantially water-immiscible solution.

It should be appreciated that the step of separating the Bayer process solutions and the substantially water-immiscible solution may be performed by any method known in the art including centrifugation.

Preferably, the step of:

seeding the Bayer process solution with alumina

is conducted after the step of:

separating the Bayer process solution and the substantially water-immiscible solution.

Preferably, the method comprises the further steps of:

contacting the substantially water-immiscible solution with a stripping solution to provide an aqueous solution of sodium hydroxide.

The stripping solution may be provided in form of water or a Bayer process liquor including condensate or lake water. Preferably, the stripping solution has a pH of at least 5.

Preferably, the method comprises the further steps of:

separating the stripping solution and the substantially water-immiscible solution.

Advantageously, the step of:

contacting the separated substantially water-immiscible solution with a stripping solution to provide an aqueous solution of sodium hydroxide;

protonates the weak acid extractant.

Advantageously, the stripping solution, after contact with the substantially water-immiscible solution can be re-used in subsequent steps in the Bayer process or in subsequent stripping steps.

The aqueous solution of sodium hydroxide may be re-used in other stages of the Bayer circuit. Depending on the concentration of sodium hydroxide, the aqueous solution may need to be pre-treated prior to subsequent use.

Advantageously, the step of stripping the sodium ions and subsequent regeneration of hydroxide may require no further chemicals for recausticisation.

In one form of the invention, the method comprises the further step of:

sonication of the Bayer process solution.

In accordance with the present invention, there is provided an organic solvent comprising an extractant in the form of a weak acid for controlling the precipitation of alumina from Bayer process solutions, wherein the precipitation of alumina comprises the steps of:

contacting the Bayer process solution with the organic solvent; and

extracting at least a portion of the sodium ions from the Bayer process solution into the organic solvent;

thereby reducing the concentration of hydroxide ions in the Bayer process solution.

In accordance with the present invention, there is provided a method for controlling the precipitation of alumina from a Bayer process solution, the method comprising the steps of:

digestion of bauxite with caustic solution;

liquid-solid separation to provide a residue and a green liquor;

precipitation of alumina from the green liquor to provide a spent liquor;

contacting the spent liquor with a substantially water-immiscible solution comprising an extractant;

extracting at least a portion of the metal cations present in the spent liquor; and

precipitation of alumina from the spent liquor.

The bauxite may be provided in the form of gibbsitic bauxite, boehmitic bauxite, diasporic bauxite or any combination thereof.

Brief Description of the Drawings

The present invention will now be described, by way of example only, with reference to three embodiments thereof, and the accompanying drawings, in which:-

Figure 1a is a schematic flow sheet of a Bayer Process circuit;

Figure 1b is a schematic flow sheet showing how a method in accordance with a first embodiment of the present invention may be utilised in a Bayer Process circuit;

Figure 1c is a schematic flow sheet showing how a method in accordance with a second embodiment of the present invention may be utilised in a Bayer Process circuit;

Figure 1d is a schematic flow sheet showing how a method in accordance with a third embodiment of the present invention may be utilised in a Bayer Process circuit;

Figure 2 is a graph showing the effect of seed loading on the precipitation of alumina from Bayer liquor;

Figure 3 is a graph showing the effect of extractant concentration on alumina yield;

Figure 4 is a graph showing the effect of temperature on the precipitation yield of alumina for extraction using *tert*-octylphenol and hexadecafluorononanol in 1-octanol;

Figure 5 is a graph showing the extraction of caustic from plant liquor as a function of time using *tert*-octylphenol/1-octanol and hexadecafluorononanol/1-octanol mixtures;

Figure 6 is a graph showing the stripping of soda from solutions of *tert*-octylphenol/1-octanol and hexadecafluorononanol/1-octanol into the aqueous phase as a function of time;

Figure 7 is a graph showing the recovery of soda from *tert*-octylphenol/1-octanol as a function of the number of volume contacts with the organic phase;

Figure 8 is a graph showing the recovery of soda from hexadecafluorononanol/1-octanol as a function of the number of volume contacts with the organic phase;

Figure 9 is a graph showing the extraction of caustic and the precipitation of hydrate from plant liquor after treatment with varying concentrations of *para*-nonylphenol in 1-octanol;

Figure 10 is a graph showing the extraction of caustic and the precipitation of hydrate from plant liquor after treatment with varying concentrations of *tert*-octylphenol in 1-octanol;

Figure 11 is a graph comparing the extraction capability of *para*-nonylphenol and *tert*-octylphenol in 1-octanol as a function of extractant concentration; and

Figure 12 is a graph comparing the stripping efficiency of *para*-nonylphenol/1-octanol and *tert*-octylphenol/1-octanol as a function of temperature.

Best Mode(s) for Carrying Out the Invention

The invention focuses on the control of alumina precipitation in the Bayer process by extraction of sodium ions from a Bayer process solution into a water immiscible solvent. By careful manipulation of the extraction reaction, the precipitation of alumina from aluminate solutions may be controlled.

It was believed that the application of the present invention, would lead to an enhancement of the reaction according to the following equation :

$$Al(OH)_4^-(aq) + Na^+(aq) + HA(org) \longrightarrow Al(OH)_3(s) + H_2O + NaA(org)$$

This equation clearly shows how hydroxide, released during the precipitation of alumina, is neutralised by the weak lipophilic agent HA with the concomitant extraction of sodium into the organic phase. This should drive the precipitation

reaction in the forward direction. Following separation, the organic phase containing NaA can be stripped with water to regenerate the caustic solution for re-use.

Seeded precipitation experiments have shown clearly that use of the present invention during alumina precipitation leads to an increase in precipitation yield compared to identical experiments performed without solvent extraction. Without being limited by theory, it is believed that seeding is advantageous for the control of precipitation properties such as particle sizes and precipitation rates.

Figure 1a shows a schematic flow sheet of the Bayer process circuit for a refinery using a single digestion circuit comprising the steps of:

digestion 12 of bauxite 14 in a caustic solution;

liquid-solid separation 16 of the mixture to residue 18 and liquor 20;

alumina precipitation 22 from the liquor 20;

separation of alumina 22 and liquor 24; and

recycling liquor 24 to digestion 12.

In accordance with a first embodiment of the present invention and best seen in Figure 1b, the liquor 24 is contacted in a solvent extraction apparatus 26 with a solution of an organic solvent 25 comprising an extractant. The aqueous layer 28 and the organic layer 30 are separated and the aqueous layer 28 seeded to induce alumina precipitation 32.

The organic layer 30 is contacted 34 with an aqueous solution 36 to back extract sodium ions from the organic layer 30 to the aqueous solution 36. The aqueous solution of increased causticity 38 may then be used in the causticisation of further bauxite or in other places in the circuit as appropriate such as, for example, as a pre-treatment step in the washing of bauxite before digestion to remove impurities or in the washing of seed or oxalate. Back extraction of the

organic layer 30 results in regeneration of the protonated form of the extractant. The extractant may then be re-used in further extraction steps.

In accordance with a second embodiment of the present invention and best seen in Figure 1c, the liquor 20 is contacted in a solvent extraction apparatus 26 with a solution of an organic solvent 25 comprising an extractant. The aqueous layer 28 and the organic layer 30 are separated and the aqueous layer 28 seeded to induce alumina precipitation 32.

The organic layer 30 is contacted 34 with an aqueous solution 36 to back extract sodium ions from the organic layer 30 to the aqueous solution 36. The aqueous solution of increased causticity 38 may then be used in the causticisation of further bauxite or in other places in the circuit as appropriate such as, for example, as a pre-treatment step in the washing of bauxite before digestion to remove impurities or in the washing of seed or oxalate. Back extraction of the organic layer 30 results in regeneration of the protonated form of the extractant. The extractant may then be re-used in further extraction steps.

In accordance with a third embodiment of the present invention and best seen in Figure 1d, the liquor 20 is seeded 21 and contacted in a solvent extraction apparatus 26 with a solution of an organic solvent 25 comprising an extractant. The precipitated alumina 27 is removed and the aqueous layer and the organic layer 30 separated.

The organic layer 30 is contacted 34 with an aqueous solution 36 to back extract sodium ions from the organic layer 30 to the aqueous solution 36. The aqueous solution of increased causticity 38 may then be used in the causticisation of further bauxite or in other places in the circuit as appropriate such as, for example, as a pre-treatment step in the washing of bauxite before digestion to remove impurities or in the washing of seed or oxalate. Back extraction of the organic layer 30 results in regeneration of the protonated form of the extractant. The extractant may then be re-used in further extraction steps.

The following Examples serve to more fully describe the manner of using the above-described invention, as well as to set forth the best modes contemplated for carrying out various aspects of the invention. It is understood that these Examples in no way serve to limit the true scope of this invention, but rather are presented for illustrative purposes.

All experiments described in Trials 1-3 were performed using synthetic liquor, containing only sodium hydroxide and dissolved alumina. The synthetic liquors had a TC of approximately 200 gL^{-1} and an A/TC of approximately 0.5 to approximate the properties of a spent liquor.

All other experiments were performed using plant liquor from the Applicant's refinery at Kwinana, Western Australia, which was blended using spent liquor (i.e. liquor ex-precipitation) and green liquor (liquor to precipitation) to achieve the desired A/TC values.

Gibbsite was used as seed for all experiments involving precipitation and these were conducted as batches using polypropylene bottles of 250 mL capacity positioned in a rotating water bath. Unless stated otherwise, 10 g of seed was used per 100 mL of liquor for precipitation experiments.

Experimental conditions and solution compositions were intended to replicate those conditions and compositions present at the backend of the alumina precipitation circuit of refineries.

1-octanol (Sigma-Aldrich) (pKa = 19.2) and all other organic solvents used were saturated with water through bulk contact prior to experimentation to minimise extraction of water into the organic phase.

1H, 1H, 9H - hexadecafluorononanol (95%, Novachem Pty Ltd, 'hexadecafluorononanol), 4-*tert*-octylphenol (97%, Sigma-Aldrich) (pKa = 10.2) and 4-nonylphenol (~85%, Sigma-Aldrich) were used as extractants. 4-nonylphenol is believed to be a mixture of branched *para*-isomers of nonylphenol and includes $HOC_6H_4C(CH_3)(CH_2CH_3)CH_2CH(CH_3)CH_2CH_3$.

Unless otherwise stated, 100 mL of liquor and 100 mL of organic phase was used and the aqueous phase, the organic phase and seed were combined and contacted for the stated time.

Where synthetic liquor was used, it was stripped with smelter grade alumina before each experiment to remove calcia and thus prevent precipitation induction time. Hydrate seed was then added to the liquor followed immediately by the organic solvent/extractant solution.

The reaction temperature was maintained at 70 °C for all experiments unless stated otherwise. Both the aqueous and organic solutions were preheated to the reaction temperature separately prior to contact.

An experimental residence time of 24 hr was chosen to allow experiments to reach equilibrium unless otherwise stated.

At the end of the contact period, precipitated alumina was collected by filtration, washed with hot water, dried in an oven at 105 °C and weighed. The aqueous filtrate was stabilised by the addition of sodium gluconate to prevent gibbsite precipitation from solution upon liquor cooling to room temperature and analysed for TC and alumina content by titration and ICP.

All experiments were performed in duplicate and the results averaged unless stated otherwise.

All solid samples from the precipitation experiments were analysed by XRD and found to consist of gibbsite only.

Trial 1

Synthetic liquor and *tert*-octylphenol in 1-octanol as a function of seeding

Experiments were conducted to determine the optimum quantity of seed required to induce precipitation of alumina from the aqueous solutions. A maximum

loading of 1 M *tert*-octylphenol in 1-octanol was employed and the seed charge was varied from 0 - 20 g and the results shown in Table 1 below.

Expt No.	Starting TC	Final TC	Ave Final TC	Al_2O_3	Ave Al_2O_3	Ave A/TC	Seed (g)	Hydrate precipitate (g)	Average (g)
1	194.15	167.8	167.61	107.32	106.63	0.6362	0	0.7	0.67
2	194.15	167.3		105.93			0	0.63	
3	194.15	174.7	173.73	55.1	54.63	0.3145	4	8.54	8.31
4	194.15	172.6		54.15			4	8.07	
5	194.15	175.1	175.11	54.22	54.08	0.3089	10	8.58	8.82
6	194.15	175.1		53.93			10	9.05	
7	194.15	173.5	174.87	52.06	52.46	0.3	20	9.35	9.16
8	194.15	176.1		52.85			20	8.97	

Table 1. Synthetic liquor and *tert*-octylphenol in 1-octanol as a function of seeding

(TC/TA = 1.0; Initial Al_2O_3 = 97.65 gL^{-1}; Initial A/TC = 0.503)

Note: Experiments 2,4,6 & 8 were duplicates of 1,3,5 & 7 respectively and the results averaged.

During normal precipitation of alumina, the overall quantity of caustic in the mixture remains constant but the TC is expected to rise slightly due to a reduction in volume of the solution as alumina is precipitated. The final TC results (Table 1) show that all of the solutions had a significant drop in TC, regardless of the amount of precipitation, indicating that the hydroxide concentration in the aqueous phase was reduced. From this observation it was inferred that extraction of sodium ions had occurred. For experiments 1 and 2, where no seed was used, only a small amount of precipitation occurred and the A/TC ratio increased from 0.50 to 0.64. Experiments 3-8, involving the addition of varying amounts of seed, produced significant amounts of alumina precipitate. The results show that alumina does precipitate in the presence of 1-octanol and indicate that it is possible to control alumina precipitation by seeding if sodium extraction and hydroxide neutralisation is used to increase precipitation yield. Furthermore, XRD analysis of the product from Experiment 6 showed it to be gibbsite.

From Figure 2, it can be seen that beyond a seed loading of 10 g, the increase in precipitation in minor. Consequently a seed charge of 10 g/100 mL was used for subsequent trials.

Trial 2

Synthetic liquor and *tert*-octylphenol in 1-octanol as a function of concentration

The results summarising the precipitation of alumina from synthetic liquor when it is treated with varying amounts of *tert*-octylphenol in 1-octanol are presented in Table 2. With increasing extractant concentration, alumina precipitation increased with a concomitant decrease in solution TC. The precipitation yield appeared to increase linearly with an increase in extractant concentration as shown in Figure 3. XRD analysis of the solid from experiment 14 showed it to consist of gibbsite.

Expt No.	Starting TC	Final TC	Ave Final TC	Al_2O_3 gL^{-1}	Ave Al_2O_3 gL^{-1}	Ave A/TC	Extractant conc (M)	Hydrate precipitate (g)	Average (g)
9	198.44	207.47	207.47	72.97	72.97	0.3516	0	4.81	4.59
10	198.44						0	4.36	
11	198.44	199.54	197.9	68.33	67.87	0.3429	0.25	5.84	5.69
12	198.44	196.27		67.41			0.25	5.56	
13	198.44	193.18	191.09	65.07	64.29	0.3364	0.5	6.59	6.49
14	198.44	189.01		63.51			0.5	6.59	

Table 2. Synthetic liquor and *tert*-octylphenol in 1-octanol as a function of concentration

(TC/TA = 1.0; Initial Al_2O_3 = 98.04; Initial A/TC = 0.494)

Note: Experiments 10, 12 and 14 were duplicates of 9, 11 and 13 and the results averaged

*Total volume of liquid was 100 mL

Trial 3

Synthetic liquor and hexadecafluorononanol in 1-octanol as a function of concentration

The results summarising the precipitation of alumina hydrate with varying amounts of 1H, 1H, 9H-hexadecafluorononanol in 1-octanol are presented in Table 3 and a comparative graph outlining the efficacy of both extractants in given in Figure 3.

Expt No.	Starting TC	Final TC	Ave Final TC	Al_2O_3 g/l	Ave Al_2O_3 g/l	Ave A/TC	Extractant conc (M)	Hydrate precipitate (g)	Average (g)
15	195.13	198.3	198.47	69.59	69.6	0.3507	0	4.52	4.56
16	195.13	198.5		69.62			0	4.61	
17	195.13	195.6	195.57	69.17	69.24	0.354	0.25	4.96	5.03
18	195.13	195.4		69.31			0.25	5.11	
19	195.13	191.9	191.39	69.1	68.79	0.3594	0.5	6.51	6.49
20	195.13	190.8		68.49			0.5	6.48	
21	195.13	181.3	181.76	65.99	66.38	0.3652	1	6.17	6.75
22	195.13	182.1		66.76			1	7.34	

Table 3. Synthetic liquor and hexadecafluorononanol in 1-octanol as a function of concentration

(TC/TA = 1.0; Initial Al_2O_3 = 96.78; Initial A/TC = 0.496)

Note: Experiments 18, 20 and 22 were duplicates of 17, 19 and 21 and the results averaged

* Total volume of liquor used was twice (200 mL) that used in previous experiments – the final average was divided by two

All of the above results show that solvent extraction of hydroxide during alumina precipitation leads to an increase in yield and that the precipitate is the desired product, gibbsite.

Trial 4

Plant liquor and 0.5 M *tert*-octylphenol and 0.5 M hexadecafluorononanol in 1-octanol

Plant liquor was adjusted using standard methods, to give an A/TC of 0.5 and a TC of 200. Precipitation experiments were performed using 10 g of seed and 0.5 M of the extractants *tert*-octylphenol and hexadecafluorononanol. All other conditions were identical to those of previous experiments.

Whilst the plant liquor contained a large amount of impurities, the results show that there is a significant increase in precipitation yield for those experiments in which solvent extraction of hydroxide was used. For example, there is a doubling in yield when *tert*-octylphenol is used and a 34% increase when the fluorononanol is used.

Sample Number	Sample name	Concentration of extractant (M)	Mass of extractant (g)	Mass of precipitated hydrate (g)	Average Mass (g)
1	No extractant	0	0	2.272	2.301
2	No extractant	0	0	2.330	
3	*tert*-octylphenol	0.5	10.317	4.459	4.479
4	*tert*-octylphenol	0.5	10.317	4.499	
5	hexadecafluorononanol	0.5	21.605	3.009	3.007
6	hexadecafluorononanol	0.5	21.605	3.005	
7	No 1-octanol	0	0	2.177	2.245
8	No 1-octanol	0	0	2.313	

Table 4. Plant liquor and *tert*-octylphenol and hexadecafluorononanol in 1-octanol as a function of concentration

It should be noted that solution A/TC ratios should not be relied upon to give an indication of the extent of precipitation. Under normal precipitation conditions with no solvent extraction, the A/TC ratio decreases because alumina leaves the solution and the solution TC increases slightly (the caustic level remains constant but solution volume decreases slightly due to alumina precipitation). However, in the case of sodium ion extraction, the TC and the alumina concentration decrease as a result of precipitation. In effect, the A/TC ratio may not change much but the level of precipitation could still be significant.

Analysis of selected spent liquor samples for Na, P, Si, oxalate, malonate, succinate and total organic carbon (TOC) content were also performed. The results for Na, P, and Si are given in Table 5 and those for oxalate, malonate, succinate and TOC in Table 6.

Sample Number	Extractant	Yield (g)	TS as Na_2CO_3 (gL^{-1})	P as P_2O_5 (gL^{-1})	Si as SiO_2 (gL^{-1})
1	1-octanol only	2.27	300	160	713
3	*tert*-octylphenol (0.5 M in 1-octanol)	4.46	295	172	764
5	Hexadecafluorononanol (0.5 M in 1-octanol)	3.01	299	160	737
7	No 1-octanol (control)	2.25	307	157	713

Table 5. ICP analysis of the liquor after extraction and gibbsite precipitation

In general terms, it would be expected that if impurities were not precipitating with the alumina or being extracted into the organic phase then their concentration in the liquor would increase during the precipitation of alumina, due to liquor volume contraction,. With respect to silicon and phosphorous, this is the observation

(Table 5). Solutions that were contacted with 1-octanol containing *tert*-octylphenol and had the greatest precipitation of alumina, had the highest concentrations of these elements after extraction. Those solutions that were contacted with hexadecafluorononanol had lower levels, although they were still higher than 1-octanol and the control experiments. A reverse trend would be expected for Na since its concentration should be a function of the strength of the Na extractant. As anticipated, the concentration of Na in the spent liquors followed the order - *tert*-octylphenol < hexadecafluorononanol < 1-octanol < control.

Sample Number	Extractant	Yield (g)	Oxalate (gL^{-1})	Malonate (gL^{-1})	Succinate (gL^{-1})	TOC (gL^{-1})
1	1-octanol only	2.27	2.82	2.49	2.34	21.9
3	*tert*-octylphenol (0.5 M in 1-octanol)	4.46	3.13	2.67	2.49	22.9
5	hexadecafluorononanol (0.5 M in 1-octanol)	3.01	3.09	2.59	2.41	22.1
7	No 1-octanol (control)	2.25	3	2.49	2.31	22.2

Table 6. Distribution of organic compounds in the liquor after extraction and gibbsite precipitation.

A similar trend was observed, as shown in Table 6, for the organic acid anions. With respect to *tert*-octylphenol, the results show that solvent extraction using n-octanol does not appear to extract Bayer liquor soluble organics into the organic phase as evidenced by the slightly higher levels found in solvent extracted liquor from which higher yields of alumina were obtained (due to volume contraction of the aqueous phase as a result of precipitation). This indicates that extraction from Bayer liquor using the extractants is selective and that concentrations of organic and inorganic impurities are unlikely to build-up in the organic phase.

Experimental work has demonstrated that the sodium ion extraction during seeded precipitation of alumina from both synthetic and plant Bayer liquors leads to a significant increase in yields of alumina. The effect has been observed using *tert*-octylphenol and hexadecafluorononanol as extractants in 1-octanol. It should be appreciated that other extractants and in particular, weak acids having an aqueous pK_a ~ 9-12 could be used as an extractant and that solvents other than 1-octanol could be utilised.

Trial 5

Plant liquor and 0.5 M *tert*-octylphenol and 0.5 M hexadecafluorononanol in 1-octanol as a function of temperature

The effect of temperature on precipitation yield for extraction is shown in Figure 4. These experiments were performed using a 1:1 ratio of liquor:organic phase, 24 hours of precipitation time and 10 g of hydrate seed. The spent liquor samples had an A/TC = 0.50 (A = 106 - 111 gL^{-1} and TC = 259 - 271 gL^{-1}). Under these conditions, maximum precipitation yields were obtained between 60-70 °C for both extraction and for the control experiments.

At temperatures higher than 60-70 °C, the yield is decreased because improved precipitation kinetics are offset by lower levels of supersaturation. At lower temperatures, the yield is also decreased because the supersaturation increase is offset by lower precipitation kinetics. Even though both extractants are effective at producing yield gains compared to control experiments, the effectiveness of hexadecafluorononanol appears to decline more sharply than that for *tert*-octylphenol at higher temperatures. The reverse trend between the two extractants is observed at lower temperatures. Notably, the difference in yields obtained for both extractants, in comparison to the control experiment, is significantly reduced at 80 °C than it is within the temperature range of 60-70 °C. There is an implication that the organic phase solubility of the sodium salt of both extractants is decreased at the higher temperature. This has important implications for caustic recovery from the organic phase by water stripping. If these extractants were to be used in a process to supersaturate spent Bayer liquor, extraction would be more effective at 60-70 °C and caustic recovery from the organic phase by water stripping should work better at temperatures higher than about 80 °C.

Trial 6

Plant liquor and 0.5 M *tert*-octylphenol and 0.5 M hexadecafluorononanol in 1-octanol as a function of time

The precipitation yield of gibbsite as a function of time is shown in Table 7. For this series of experiments, the starting Al_2O_3 concentration was 99-107 gL^{-1} and the starting TC was 201-214 gL^{-1}. The A/TC ratio was kept constant at 0.50.

After both four and eight hours, where 0.5 M *tert*-octylphenol was the extractant, a significant amount of precipitation was observed compared to the control experiments, which is indicative of a higher level of induced supersaturation.

Extractant	Time (hr)			
	4	8	24	48
No octanol (control)	0.07 g	0.18 g	2.24 g	2.02 g
hexadecafluorononanol (0.5 M in 1-octanol)			3.07 g	3.07 g
tert-octylphenol (0.5 M in 1-octanol)	1.39 g	2.51 g	4.48 g	4.44 g

Table 7. Plant liquor and 0.5 M *tert*-octylphenol and 0.5 M hexadecafluorononanol in 1-octanol as a function of time

However, there was little change in yield benefit after 8 hours where *tert*-octylphenol was used *i.e.* for 8, 24 and 48 hours the yields were 2.3, 2.2 and 2.4 g respectively greater than the respective controls. This trend was also consistent with the weaker extractant hexadecafluorononanol, which did not produce a significantly higher yield after 48 hours than that obtained at 24 hours. Without being limited by theory, it is believed that the solvent extraction of soda from Bayer liquor may lead to an increase in the kinetics of gibbsite precipitation. Not only is hydroxide neutralised to increase alumina solution supersaturation, but sodium ions are also removed from the liquor. Sodium ions may be expected to have an inhibitory effect on kinetics since they concentrate on the gibbsite seed surface and need to be displaced during the normal course of precipitation. Hence, a lower sodium ion activity could favour increased kinetics.

When the solids from these experiments were analysed, those samples obtained post solvent extraction did not contain any significantly higher levels of soda or

silica than observed for the controls despite the higher yields (*cf.* XRF results of 0.237 % Na_2O, 0.0036 % SiO_2 for *tert*-octylphenol (24 hr) solids compared to 0.211 % Na_2O, 0.0061 % SiO_2 for control (24 hr) solids). This result is important because it demonstrates that the increased alumina yields obtained using solvent extraction of soda do not come at the expense of product purity.

Trial 7

Plant liquor and *tert*-octylphenol in 1-octanol as a function of A/TC ratio

A number of experiments were performed towards establishing the effect of change in starting A/TC ratio on yields obtained using extraction with 0.5M *tert*-octylphenol. The results for starting A/TC ratios of 0.5 and 0.6 are given in Table 8. For this series of experiments, the starting Al_2O_3 concentration was 99-128 gL^{-1}, the starting TC was 201-213 gL^{-1}, the time was 24 hr and the temperature was 70 °C.

Initial A/TC ratio	Gibbsite precipitated (g)		
	No octanol (control)	Octanol only	*tert*-octylphenol (0.5M) in octanol
0.5	2.25	2.27	4.46
0.6	4.25	4.13	6.59

Table 8. Plant liquor and *tert*-octylphenol in 1-octanol as a function of A/TC ratio

The solvent extracted samples gave consistently higher yields than the controls, although the gain above the control was only slightly more at A/TC 0.6 (gain 2.3 g) than the gain at A/TC 0.5 (2.2 g). It should be possible to increase the degree of supersaturation of liquors which have a wide range of A/TC ratios, providing that appropriate volume ratios of organic phase to liquor are used at specified extractant loadings. The examples given thus far have used volume ratios of 1:1; however, greater supersaturation levels could be generated and hence higher overall yields could be obtained, by using higher extractant ratios.

Trial 8

Plant liquor and *tert*-octylphenol and hexadecafluorononanol in 1-octanol as a function of liquor to solvent ratio

Experiments were performed using 3:1 volume ratios of organic phase, containing 0.5 M each of *tert*-octylphenol and hexadecafluorononanol, to plant liquor to demonstrate that greater increases in yield can be obtained by using higher ratios of extractant to liquor (Table 9). For these experiments, the initial Al_2O_3 concentration was 102.53 gL^{-1}; the initial A/TC = 0.480 and 200 gL^{-1} of hydrate was used as seed. Since 150 mL of organic phase was used to 50 mL of liquor, the final yields were multiplied by a factor of 20 to provide the gL^{-1} values. Experiments 3 & 5 are duplicates of 2 & 4 respectively and the results have been averaged.

From this data, it is clear that using higher volume ratios of organic phase to liquor results in additional increases in alumina yield. For example, in the case of *tert*-octylphenol, using a 1:1 volume ratio of *tert*-octylphenol solution:plant liquor gave an approximate yield of 22.3 gL^{-1} of hydrate over the control whereas using a 3:1 volume ratio of *tert*-octylphenol solution:plant liquor gave a 59.6 gL^{-1} yield increase over the control.

Expt No.	Organic solvent	Starting TC	Final TC	Average final TC	Final Al_2O_3 (gL^{-1})	Average Al_2O_3 (gL^{-1})	Hydrate precipitated (g)	Average yield of hydrate (gL^{-1})
1	1-octanol	213.79	215.44	215.44	90.21	90.21	0.56	11.3
2	*tert*-octylphenol (0.5 M in 1-octanol)	213.79	170.31	168.23	66.71	65.90	3.53	70.9
3		213.79	166.14		65.08		3.56	
4	hexadecafluorononanol (0.5 M in 1-octanol)	213.79	191.45	195.48	79.59	81.77	1.69	32.1
5		213.79	199.50		83.94		1.52	

Table 9. Plant liquor and *tert*-octylphenol and hexadecafluorononanol in 1-octanol as a function of liquor to solvent ratio

A similar trend was observed for hexadecafluorononanol, where a volume ratio of 1:1 gave a yield of 7.6 gL^{-1} over the control and a volume ratio of 3:1 gave 20.8 gL^{-1} over the control. These results demonstrate that by using larger volumes, of organic phase to liquor, it is possible to extract more soda from the

liquor and therefore increase the degree of supersaturation to obtain greater yield benefits.

Trial 9

Plant liquor and 0.5 M *tert*-octylphenol in 1-octanol as a function of the number of contacts

This trial used the same plant liquor as in Trial 8 and was performed so that a comparison could be made between the effectiveness of three separate 1:1 volume ratio extractions, using the same plant liquor, and one extraction using a 3:1 volume ratio of organic phase to liquor. The comparison was made based upon recovered yields after each precipitation run. The volume of plant liquor and organic phase used in the experiments was 100 mL. The results are presented in Table 10.

	Yield after first contact (g)	Yield after second contact (g)	Yield after third contact (g)
Experiment 1	2.91	1.85	1.75
Experiment 2 (duplicate)	2.95	1.86	1.75
Control experiment	0.56	-	-
Overall yield gain (average of Expts 1&2 minus control)	2.37	1.85	1.75

Table 10. Plant liquor and 0.5 M *tert*-octylphenol in 1-octanol as a function of the number of contacts

These results demonstrate that it is possible to extract further soda from the same batch of plant liquor to obtain increased yields of alumina by seeding after each extraction phase. The total cumulative additional yield of hydrate, after three series of sequential extraction/precipitation experiments, was 5.97 g/ 100 mL (59.7 gL^{-1}) (after subtracting the quantity of precipitate obtained from the initial control experiment using uncontacted liquor). As a comparison, the amount of hydrate obtained from Trial 8, for a 3:1 volume contact using the same quantity of *tert*-octylphenol in 1-octanol, was 59.6 gL^{-1} more than that obtained from the corresponding control experiment. Hence, it is concluded from these experiments that a 3:1 volume ratio contact of organic extractant:plant liquor is similar to three separate 1:1 contacts in terms of added yield benefits after seeded precipitation after each extraction.

Trial 10

Plant liquor and 0.5 M *tert*-octylphenol and 0.5 M hexadecafluorononanol in 1-octanol as a function of time

Kinetic experiments were performed to establish the period to reach equilibrium when caustic is extracted from plant liquor using 0.5 M of the organic extractants *tert*-octylphenol and hexadecafluorononanol in 1-octanol. The experiments were performed in an open 3 L reaction vessel made from stainless steel ,equipped with a water jacket to maintain temperature at 70 °C. The mixtures were stirred using an overhead impeller, the blades of which were positioned so that they were at the interface of the organic/aqueous phases. The organic/extractant mixtures (300 mL), which had been equilibrated to temperature in a separate container, were added to the aqueous plant liquor (300 mL). The resulting mixtures were stirred vigorously and small aliquots of the aqueous phase withdrawn at regular intervals for analysis. The results, for both extractants in 1-octanol, are presented in Figure 5 which shows the total caustic (expressed as Na_2CO_3) in the plant liquor as a function of time. Whilst the experimental time frame was 120 min, results for times longer than 10 min are not included in the graph since they were no different to the values at 10 minutes. The A/TC values, which are representative of supersaturation, are also included in the graph on the far right vertical axis.

The results show that the extraction of soda from the plant liquor, using either *tert*-octylphenol and hexadecafluorononanol, occurs very rapidly and a state of equilibrium (where the curves flatten out) is attained within 30 seconds.

Trial 11

Stripping of 0.5 M *tert*-octylphenol and 0.5 M hexadecafluorononanol in 1-octanol as a function of time

Kinetic experiments were performed to establish the length of time taken to reach equilibrium when caustic is recovered from the organic phases of 0.5 M *tert*-

octylphenol in 1-octanol and 0.5 M hexadecafluorononanol in 1-octanol by contacting with water. The same equipment, experimental conditions and volumes were employed as described in Trial 10. The resulting mixtures were stirred vigorously and small aliquots of the aqueous phase were withdrawn at regular intervals for analysis. The results, for both extractants in 1-octanol, are presented in Figure 6 which shows the total caustic (expressed as Na_2CO_3) increases in the aqueous layer as a function of time. Values up to 120 minutes were obtained but are not shown on the graph because they were no different to those at 30 minutes. The results are similar to the extraction kinetics experiments in that the stripping reaction is rapid and reaches equilibrium within 30 seconds.

Trial 12

Stripping of 0.75 M *tert*-octylphenol in 1-octanol as a function of caustic recovery

A bulk organic phase, generated by contacting 0.75 M *tert*-octylphenol in 1-octanol with plant liquor from ex-precipitation, was used in these experiments. The organic phase was analysed for Na content and found to contain 0.623 M of Na expressed as 33.0 gL^{-1} of Na_2CO_3.

The stripping experiments were performed at 70 °C in a 3 L capacity stainless steel reactor, equipped with a four blade impeller. The impeller was rotated at 450 rpm for 10 min to affect phase contact. Prior to contact, the organic (initially 600 mL) and aqueous phases (initially 300 mL) were preheated to 70 °C. Following contact, the phases were separated and a sub-sample of the aqueous phase was withdrawn for analysis. The remaining aqueous phase was contacted with twice the volume of fresh loaded organic and the procedure repeated until a total of six independent contacts, using the same aqueous strip, had been conducted. The results are presented in Figure 7, which displays the caustic content of the aqueous phase as a function of the number of volume contacts with the soda loaded organic (1-octanol) phase. The diagram also contains a theoretical line which shows the level of caustic in the aqueous phase which is representative of 100% stripping efficiency.

It is apparent from the data that it is possible to extract soda from the organic phase to recover a reasonably concentrated stream of caustic (*cf.* TC > 130 gL^{-1}, $[OH^-]$ > 2.4 M) by performing a number of sequential stripping steps using the same aqueous phase. However, as shown in the graph, the stripping is not complete and an amount of soda still remains in the organic phase. From a process perspective, much of this remaining soda could be recovered utilising a setup employing counter current stripping, where stripped organic phase is contacted further with fresh aqueous phase, which should increase the efficiency of the operation.

Importantly, these stripping experiments have demonstrated that a significant amount of caustic can be recovered from the organic phase, containing *tert*-octylphenol, which could then be recycled back into the Bayer process after further concentration using conventional procedures such as evaporation.

Trial 13

Stripping of hexadecafluorononanol in 1-octanol as a function of caustic recovery

A bulk organic phase, generated by contacting 0.50 M hexadecafluorononanol in 1-octanol with plant liquor from ex-precipitation, was used in these experiments. The organic phase was analysed and found to contain a sodium content of 13.24 gL^{-1} expressed as Na_2CO_3.

The stripping experiments, utilising de-ionised water, were performed in an identical manner to those in Trial 12 and the results are shown in Figure 8. Recovery of caustic from Na loaded solutions of hexadecafluorononanol in 1-octanol appears to be more efficient than for *tert*-octylphenol. It is believed that this is related to the lower extraction strength of hexadecafluorononanol. It is evident from the stripping curve that extrapolation of the curve to contact ratios higher than 10 volume equivalents should result in the recovery of caustic above 100 gL^{-1} of Na_2CO_3.

Even though stripping for caustic recovery is more efficient for hexadecafluorononanol, than it is for *tert*-octylphenol, *tert*-octylphenol is more effective than hexadecafluorononanol at extracting soda from Bayer liquor (on a molar equivalent basis) and its use results in greater alumina yield gains.

Trial 14

Stripping of *tert*-octylphenol and hexadecafluorononanol in 1-octanol as a function of caustic recovery

A series of tests were performed to establish whether caustic could be recovered from the organic phases containing soda by stripping into refinery process streams rather than deionised water. Process streams such as lake water, which contain appreciable amounts of caustic (since they are derived from residue washing), are recycled into the refinery Bayer liquor during the normal course of operation. Stripping caustic into these would reduce the pure water input into the refinery and save on the cost of extra evaporation.

The stripping experiments were conducted in polypropylene bottles using a total volume of 200 mL and a time of 24 hr. As an example, a volume ratio of organic:aqueous of 2:1 consisted of 135 mL of organic to 65 mL of aqueous phases. The temperature was held constant at 90 °C and the initial soda content of the lake water was 33.6 gL^{-1} expressed as Na_2CO_3. The results are given Table 11.

Volume contact organic : aqueous	Caustic as Na2CO3 (g/L)		
	No extractant	0.50 M HDFN	0.50 M TOP
0	33.6	33.6	33.6
2	35.8	51.2	59.7
4	39.3	67.5	75.8

Table 11. Stripping of *tert*-octylphenol and hexadecafluorononanol in 1-octanol as a function of caustic recovery

These results demonstrate that it is possible to recover appreciable amounts of soda from the organic phases containing *tert*-octylphenol and hexadecafluorononanol by stripping into refinery lake water. In the case of *tert*-

octylphenol, the caustic content of the lake water was more than doubled by one single contact using a 4:1 ratio of organic:aqueous phases. The control experiment for the series was 1-octanol which had been contacted with Bayer liquor. The control extracted a small amount of soda from the liquor as evidenced by the small increase in caustic content of the lake water upon stripping.

Trial 15

Plant liquor and *para*-nonylphenol in 1-octanol and *iso*-octanol

Trials were conducted using *para*-nonylphenol under conditions designed to simulate more closely the situation that would occur in the adoption of the present invention at a refinery where spent liquor would be supersaturated by solvent extraction of soda and then fed through a seeded precipitation circuit in the absence of organic solvent. As such, in each of the following experiments, plant liquor with an A/TC value of 0.5 was contacted with specified quantities of the extractant in 1-octanol (1:1 ratio of organic phase:aqueous) in the absence of seed. After a contact time of 10 minutes with rapid stirring, the phases were separated and the treated plant liquor was then seeded and allowed to form precipitate for 24 hr at 70 °C. The amount of liquor used in each seeding experiment was 200 mL, the added seed was 20 g of hydrate and the experiments were conducted in 250 mL polypropylene bottles placed in a rotating holder in a water bath to maintain temperature. The results are shown in Figure 9 which displays the TC drop of the liquor after extraction (before seeding) and the yield of gibbsite obtained after precipitation for 24 hr.

Precipitation results for *para*-nonylphenol concentrations of > 1 M were not obtained because the liquors were so highly supersaturated that it was difficult to prevent spontaneous precipitation before phase separation was effected. However, TC values were obtained after liquor stabilisation by the addition of a known amount of sodium gluconate, which is a precipitation inhibitor, just after phase separation but before analysis.

The results show that *para*-nonylphenol is a strong extractant and its use to supersaturate low A/TC liquor results in large yield increases compared to the control experiment where 1-octanol was used. Its use at a concentration of 1M resulted in a yield increase of 62.2 gL^{-1} of hydrate over that of the control experiment.

Importantly, mixtures of *para*-nonylphenol, which is a liquid at room temperature, in 1-octanol showed much improved phase separation behaviour, and lower viscosity, after mixing with plant liquor than those of *tert*-octylphenol and hexadecafluorononanol in 1-octanol. These factors enable *para*-nonylphenol to be used in higher concentrations in 1-octanol than either *tert*-octylphenol or hexadecafluorononanol.

A further test was performed to determine whether 1-octanol could be replaced by an industrial grade *iso*-octanol solvent, Exxal 8 (ExxonMobil), as a carrier for *para*-nonylphenol. Two tests were performed under identical conditions to the *para*-nonylphenol concentration experiments and using liquor with a starting composition very close to that use for the 1-octanol runs. Two concentrations of *para*-nonylphenol in Exxal 8 were tested and the results, which are presented in Table 12, are compared with the identical experiments using 1-octanol.

	[*para*-nonylphenol] (M)	TC	TC decrease
Starting liquor A/TC = 0.5	-	207.94	-
n-octanol	0.40	185.01	23.51
	0.60	173.75	36.14
Starting liquor A/TC = 0.5	-	213.34	-
Exxal 8	0.40	194.96	22.93
	0.60	187.50	34.19

Table 12. Comparison of the extraction efficiency of *para*-nonylphenol in 1-octanol and Exxal 8

The results show that Exxal 8 can be used as a replacement for 1-octanol as the carrier solvent for *para*-nonylphenol.

Trial 16

Comparison of *para*-nonylphenol and *tert*-octylphenol

These experiments were performed in an identical manner to those of Trial 15 with the exception that *tert*-octylphenol was used as the extractant instead of *para*-nonylphenol. The experimental conditions were as described for Trial 15. The results are presented in Figure 10.

The results show that the *tert*-octylphenol / 1-octanol mixture extracted a considerable amount of soda from the liquor and when the re-supersaturated liquor was seeded, high yields were obtained in comparison to liquor which had not under gone prior extraction.

A comparison of the extraction strength of *tert*-octylphenol / 1-octanol and *para*-nonylphenol / 1-octanol is given in Figure 11. It is evident that both extractants have similar capabilities at lower concentrations but *para*-nonylphenol appears to be superior at concentrations above 0.5 M.

Trial 17

Comparison of *para*-nonylphenol and *tert*-octylphenol as a function of solvent

Trials were conducted to establish the efficacy of both *tert*-octylphenol and *para*-nonylphenol as extractants using commercially available diluents. Various solutions of *tert*-octylphenol and *para*-nonylphenol in commercially available *iso*-octanol solvent ('Exxal 8', ExxonMobil) and three hydrocarbon diluents, ('Isopar L', 'Escaid 110' and 'Solvesso 150', ExxonMobil). Solvesso 150 solvent is 99 % aromatic in nature and the Escaid 110 and Isopar L solvents are predominantly linear hydrocarbon solvents.

The experiments were performed using 20 vol % Exxal 8 in 80 % diluent. Each extractant was used at a concentration of 0.5 M and 600 mL of the organic phase

containing the extractant was contacted with an equal volume of plant liquor for 10 min at 60 °C. The starting A/TC of the plant liquor was 0.5. After contact, both phases were separated and the aqueous phase analysed for caustic content. The results are presented in Table 13.

Apparent from Table 13 is that *para*-nonylphenol in the Exxal 8/diluent mixtures acted as a more efficient extractant than *tert*-octylphenol. When the mixtures containing *tert*-octylphenol were contacted with the plant liquor, they either formed highly viscous emulsions which did not separate upon standing or, in the case of the *tert*-octylphenol/Exxal/Solvesso mixture, a solid emulsion. In contrast. all of the mixtures containing *para*-nonylphenol were capable of extracting significant amounts of soda with the mixture containing Isopar L being marginally better than that containing Escaid 110 and the Escaid 110 being considerably better than that containing Solvesso 150. The results for extraction with 0.5 M *para*-nonylphenol in Exxal 8/Isopar L and for 0.5 M *para*-nonylphenol in 1-octanol (Figure 9) were similar.

Overall, these results suggest that *para*-nonylphenol may be used with a wider variety of solvents than *tert*-octylphenol.

Volume ratio	**Organic Volume (mL)**		**Extractant**	**Final TC of liquor (g/L of Na_2CO_3)**	**TC extracted (g/L Na_2CO_3)**
20% Exxal 8 in 80% diluent	**600 mL of mixed organic**				
Initial Liquor with A/TC = 0.50 /TC = 212.95					
1 to 4	Exxal 8	Isopar L	No extractant (control)	212.38	0.57
	120.0	480.0			
1 to 4	Exxal 8	Isopar L	0.50M PNP	184.71	28.24
	120.0	480.0			
1 to 4	Exxal 8	Solvesso 150	0.50M PNP	188.74	24.21
	120.0	480.0			
1 to 4	Exxal 8	Escaid 110	0.50M PNP	186.12	26.83
	120.0	480.0			
1 to 4	Exxal 8	Isopar L	0.50M TOP	No data could be obtained as mixture formed viscous emulsion	
	120.0	480.0			
1 to 4	Exxal 8	Solvesso 150	0.50M TOP	No data could be obtained as mixture formed solid emulsion	
	120.0	480.0			
1 to 4	Exxal 8	Escaid 110	0.50M TOP	No data could be obtained as mixture formed viscous emulsion	
	120.0	480.0			

Table 13. Comparison of *para*-nonylphenol and *tert*-octylphenol as a function of solvent

Trial 18

Comparison of the stripping efficiency with *para*-nonylphenol in 1-octanol and *tert*-octylphenol in 1-octanol as a function of temperature

Bulk organic phases were generated by treating 0.8 M *tert*-octylphenol/1-octanol and 0.8 M *para*-nonylphenol/1-octanol with plant liquor from ex-precipitation in a 1:1 ratio. The organic phases were analysed for Na content and were found to contain 34.6 gL^{-1} of Na, expressed as Na_2CO_3, for the *para*-nonylphenol/1-octanol extraction, and 33.0 gL^{-1} of Na, expressed as Na_2CO_3,, for the *tert*-octylphenol/1-octanol extraction.

Experiments were performed using a 4:1 volume contact of each organic phase with water at different temperatures. Each of the mixtures was initially heated to a temperature of 50 °C and allowed to equilibrate with stirring for 10 min. A subsample containing approximately equal volumes of aqueous and organic phases was withdrawn and the aqueous phase was analysed. The procedure was repeated at a number of temperatures up to 85 °C using the same batch of each extractant/1-octanol/aqueous mixture. The results are presented in Figure 12.

The results show that at the temperatures measured, *para*-nonylphenol/1-octanol is stripped more efficiently than *tert*-octylphenol/1-octanol, although there is a narrowing of the gap at higher temperatures. At 85 °C, the stripping efficiency of *para*-nonylphenol/1-octanol is 45.5 % compared to 39.6 % for *tert*-octylphenol/1-octanol. The efficiency of the stripping for both extractants increases with temperatures which is a reflection of the lower solubility of the sodium salt of the extractants in the organic phase at increased temperature.

Overall, *para*-nonylphenol appears to be a more versatile extractant than *tert*-octylphenol as solutions maybe prepared at higher concentrations, it is compatible with more industrial solvents and caustic can be recovered from it more efficiently by stripping into an aqueous phase than it can for *tert*-octylphenol.

Trial 19

The recovery of soda from *para*-nonylphenol/Exxal 8/hydrocarbon diluent mixtures by stripping with water

Experiments were performed to determine the efficiency of soda recovery, by water stripping, from the *para*-nonylphenol/Exxal 8/diluent mixtures which were contacted with plant liquor in Trial 17.

The tests were conducted in plastic bottles, positioned in a bottle roller placed in a water bath at 70 °C for a period of 24 hr. The ratio of organic phase to water was 1:1 and the initial concentration of soda in the organic phase was determined by acid stripping. The results for the three tests conducted are presented in Table 14 and show that soda can be stripped with high efficiency from the Exxal 8/diluent mixtures using 1:1 volume ratios of organic to aqueous phase.

	Total caustic in organic phase as gL^{-1} Na_2CO_3 (by HNO_3 stripping)	Total caustic stripped into water (as gL^{-1} Na_2CO_3)	stripping efficiency
HNO_3 blank	0.6	0.1	
0.50 M *para*-nonylphenol/Exxal 8/Isopar L	23.9	22.4	94 %
0.50 M *para*-nonylphenol/Exxal 8/Solvesso 150	20.6	23.1	100 %
0.50 M *para*-nonylphenol/Exxal 8/Escais 110	23.6	22.0	93 %

Table 14. The recovery of soda from *para*-nonylphenol/mixed solvent mixtures by stripping with water at 70 °C.

Trial 20

Stripping of soda loaded *tert*-octylphenol/1-octanol and *para*-nonylphenol/1-octanol organic solutions by refinery lake water and de-ionised water.

Experiments were performed to study the efficiency of recovering soda from organic extraction mixtures by contact with refinery lake water and de-ionised water.

Organic solutions were prepared in bulk by contacting plant liquor with 0.6 M *tert*-octylphenol in 1-octanol and by contacting plant liquor with 0.6 M *para*-nonylphenol in 1-octanol. The total soda content of each organic phase was

determined by stripping the phase with dilute nitric acid followed by ICP- OES analysis. Each of the organic mixtures was then contacted with refinery lake water for three hours at 70 °C or with de-ionised water under the same conditions. The volume ratio of organic to aqueous phase was 4:1 and the experiments were conducted in duplicate. The results are presented in Table 15.

The results show that soda can be recovered from the organic phase by stripping using either refinery lake water or deionised water with only a small difference in efficiency between the two stripping solutions. Further, both extractants appeared to strip equally well with only a small difference in favour of *para*-nonylphenol using lake water. As discussed in Trial 12, the total causticity of the stripping solutions could be increased further by performing multiple contacts of fresh soda loaded organic phase with the same stripping solution.

Sample ID	Description	$[Na]_{org}$ (gL^{-1} Na_2CO_3)	$[Na]_{strip\ so39.0In}$ (gL^{-1} Na_2CO_3)	Increase in strip solution concentration	Stripping Efficiency
Lake water	Lake water (blank)		39.0		
DI water	DI water (blank)		1.3		
tert-octylphenol/ lake water	0.60 M *tert*-octylphenol in 1-octanol + lake water at 70 °C (org:aq 4:1)	28.6	77.0	38.0	33.2 %
tert-octylphenol/ lake water			76.9	37.9	33.1 %
tert-octylphenol/DI water	0.60 M *tert*-octylphenol in 1-octanol + DI water at 70 °C (org:aq 4:1)		43.6	42.6	37.2 %
tert-octylphenol/DI water			42.7	41.4	36.2 %
para-nonylphenol/ lake water	0.60 M *para*-nonylphenol in 1-octanol + lake water at 70 °C (org:aq 4:1)	30.2	80.3	41.3	34.2 %
para-nonylphenol/ lake water			79.4	40.4	33.4 %
para-nonylphenol/ DI water	0.60 M *para*-nonylphenol in 1-octanol + lake water at 70 °C (org:aq 4:1)		43.1	41.8	34.6 %
para-nonylphenol/ DI water			44.4	45.4	37.6 %

Table 15 The recovery of soda from *tert*-octylphenol/1-octanol and *para*-nonylphenol/1-octanol mixtures by stripping with refinery lake water and de-ionised water.

The Claims Defining the Invention are as Follows:

1. A method for controlling the precipitation of alumina from a Bayer process solution, the method comprising the steps of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant;

extracting a metal cation present in the Bayer process solution into the substantially water-immiscible solution;

thereby reducing the concentration of hydroxide ions in the Bayer process solution.

2. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 1, wherein the method comprises the step of:

precipitation of alumina in the Bayer process solution.

3. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of claims 1 and 2, wherein the method comprises the step of:

seeding the Bayer process solution with alumina.

4. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 3, wherein, the step of:

seeding the Bayer process solution with alumina

is conducted prior to the step of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant.

5. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 3, wherein, the step of:

seeding the Bayer process solution with alumina

is conducted after the step of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant.

6. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the alumina is provided in the form of gibbsite, boehmite, bayerite, doyleite, diaspore and/or nordstrandite.

7. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the metal cation is a sodium ion.

8. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the extractant is provided in the form of a weak acid.

9. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 8, wherein the extraction of the metal ion into the substantially water-immiscible solution is accompanied by the transfer of a proton from the substantially water-immiscible solution into the Bayer process solution.

10. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 8 or claim 9, wherein the weak acid extractant comprises at least one polar group with an ionisable proton with a pKa of between about 9 and about 13.

11. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the extractant is a straight chain, branched chain or cyclic hydrocarbon, a halogenated hydrocarbon, an aliphatic or aromatic ether or an alcohol with more than 6 carbon atoms.

12. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the extractant comprises an alcohol or phenol functional group.

13. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the extractant is selected from the group comprising 1H,1H-perfluorononanol, 1H,1H,9H-hexadecafluorononanol, 1,1,1-trifluoro-3-(4-*tert*-octylphenoxy)-2-propanol, 1,1,1-trifluoro-2-(*p*-tolyl)*iso*propanol, 1-(*p*-tolyl)-2,2,2-trifluoroethanol, hexafluoro-2-(*p*-tolyl)isopropanol, 2-(methyl)-2-(dodecyl)tetradecanoic acid, 3-(perfluorohexyl)propenol and 1-(1,1,2,2-tetrafluoroethoxy)-3-(4-*tert*-octylphenoxy)-2-propanol, *tert*-octylphenyl, *para*-nonylphenol, *para-tert*-butylphenol, *para-tert*-amylphenol, *para*-heptylphenol, *para*-octylphenol, *para*-(alpha,alpha-dimethylbenzyl)phenol (4-cumylphenol), 2,3,6-trimethylphenol, 2,4-di-*tert*-butylphenol, 3,5-di-*tert*-butylphenol, 2,6-di-*tert*-butylphenol, 2,4-di-*tert*-pentylphenol (2,4-di-*tert*-amylphenol), 4-sec-butyl-2,6-di-*tert*-butylphenol, 2,4,6-tri-*tert*-butylphenol, 2,4-bis(alpha,alpha-dimethylbenzyl)phenol (2,4-dicumylphenol) and other alkylated phenols or mixtures thereof.

14. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the substantially water-immiscible solution is the extractant.

15. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the acidic form of the extractant is substantially insoluble in water.

16. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the deprotonated form of the extractant is substantially insoluble in water.

17. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the substantially water-immiscible solution comprises a phase transfer catalyst.

18. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 17, wherein the phase transfer catalyst is selected from the group comprising lipophilic quaternary ammonium or phosphonium salts or organic macrocycles such as crown ethers, calixarenes, calixarene-crown ethers, spherands and cryptands.

19. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the substantially water-immiscible solution comprises a complexing ligand adapted to synergistically enhance sodium ion extraction, and/or to additionally extract impurities from Bayer liquor and enhance precipitation in a secondary manner.

20. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the step of contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant is performed in a process side stream.

21. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the Bayer process includes the steps:

digestion of bauxite with caustic solution;

liquid-solid separation to provide a residue and a liquor; and

precipitation of alumina from the liquor; and

the steps of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant; and

extracting at least a portion of the metal cations present in the Bayer process solution into the substantially water-immiscible solution;

are conducted prior to the step of:

precipitation of alumina from the liquor.

22. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the Bayer process includes the steps:

digestion of bauxite with caustic solution;

liquid-solid separation to provide a residue and a liquor; and

precipitation of alumina from the liquor; and

the steps of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant; and

extracting at least a portion of the metal cations present in the Bayer process solution into the substantially water-immiscible solution;

are conducted after the step of:

precipitation of alumina from the liquor.

23. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of claims 1 to 21, wherein the Bayer process includes the steps:

digestion of bauxite with caustic solution;

liquid-solid separation to provide a residue and a liquor; and

precipitation of alumina from the liquor; and

the steps of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant; and

extracting at least a portion of the metal cations present in the Bayer process solution into the substantially water-immiscible solution;

are conducted during the step of:

precipitation of alumina from the liquor

24. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the substantially water-immiscible solution is an organic liquid, a combination of organic liquids or an ionic liquid.

25. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 24, wherein the organic liquid is substantially non-polar.

26. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 24 or 25, wherein the organic liquid is a high boiling organic liquid with a low vapour pressure at Bayer process temperatures.

27. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of claims 24 to 26, wherein the organic liquid is a straight chain, branched chain or cyclic hydrocarbon, a halogenated hydrocarbon, an aliphatic or aromatic ether or alcohol with more than 4 carbon atoms.

28. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 24, wherein the organic liquid is selected from the group comprising benzene, toluene, xylene, stilbene, 1-octanol, 2-octanol, 1-decanol, *iso*-octyl alcohol (such as that commercially available as Exxal 8 from ExxonMobil), iso-nonylalcohol (such as that commercially available as Exxal 9 from ExxonMobil), *iso*-decanol, *iso*-tridecanol, 2-ethyl-1-hexanol, kerosene and other hydrocarbons commercially available under the names Escaid 100, Escaid 110, Escaid 240, Escaid 300, Isopar L, Isopar M, Solvesso 150 from ExxonMobil) and mixtures thereof.

29. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of claims 24 to 28, wherein the organic liquid solvates the extractant in both its acid and sodium salt forms.

30. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the step of:

contacting the Bayer process solution with a substantially water-immiscible solution comprising an extractant;

comprises agitating the Bayer process solution and the substantially water-immiscible solution by shaking, stirring, rolling and sparging.

31. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of the preceding claims, wherein the method comprises the further step of:

separating the Bayer process solution and the substantially water-immiscible solution.

32. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 31, wherein the step of:

seeding the Bayer process solution with alumina,

is conducted after the step of:

separating the Bayer process solution and the substantially water-immiscible solution.

33. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 31 or claim 32, wherein the method comprises the further step of:

contacting the separated substantially water-immiscible solution with a stripping solution to provide an aqueous solution of sodium hydroxide.

34. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 33, wherein the method comprises the further step of:

separating the stripping solution and the substantially water-immiscible solution.

35. A method for controlling the precipitation of alumina from a Bayer process solution according to claim 33 or claim 34, wherein the stripping solution, after contact with the substantially water-immiscible solution is re-used in subsequent steps in the Bayer process or in subsequent stripping steps.

36. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of claims 33 to 35, wherein the stripping solution has a pH of at least 5.

37. A method for controlling the precipitation of alumina from a Bayer process solution according to any one of claims 33 to 36, wherein the stripping solution is prepared from streams in the Bayer process circuit.

38. An organic solvent comprising an extractant in the form of a weak acid for controlling the precipitation of alumina from a Bayer process solution, wherein the precipitation of alumina comprises the steps of:

contacting the Bayer process solution with the organic solvent; and

extracting at least a portion of the sodium ions from the Bayer process solution into the organic solvent;

thereby reducing the concentration of hydroxide ions in the Bayer process solution.

39. A method for controlling the precipitation of alumina from a Bayer process solution as hereinbefore described with reference to the accompanying Examples.

40. A method for controlling the precipitation of alumina from a Bayer process solution as hereinbefore described with reference to the accompanying Figures.

41. An organic solvent comprising an extractant in the form of a weak acid for controlling the precipitation of alumina from a Bayer process solution as hereinbefore described with reference to the accompanying Examples.

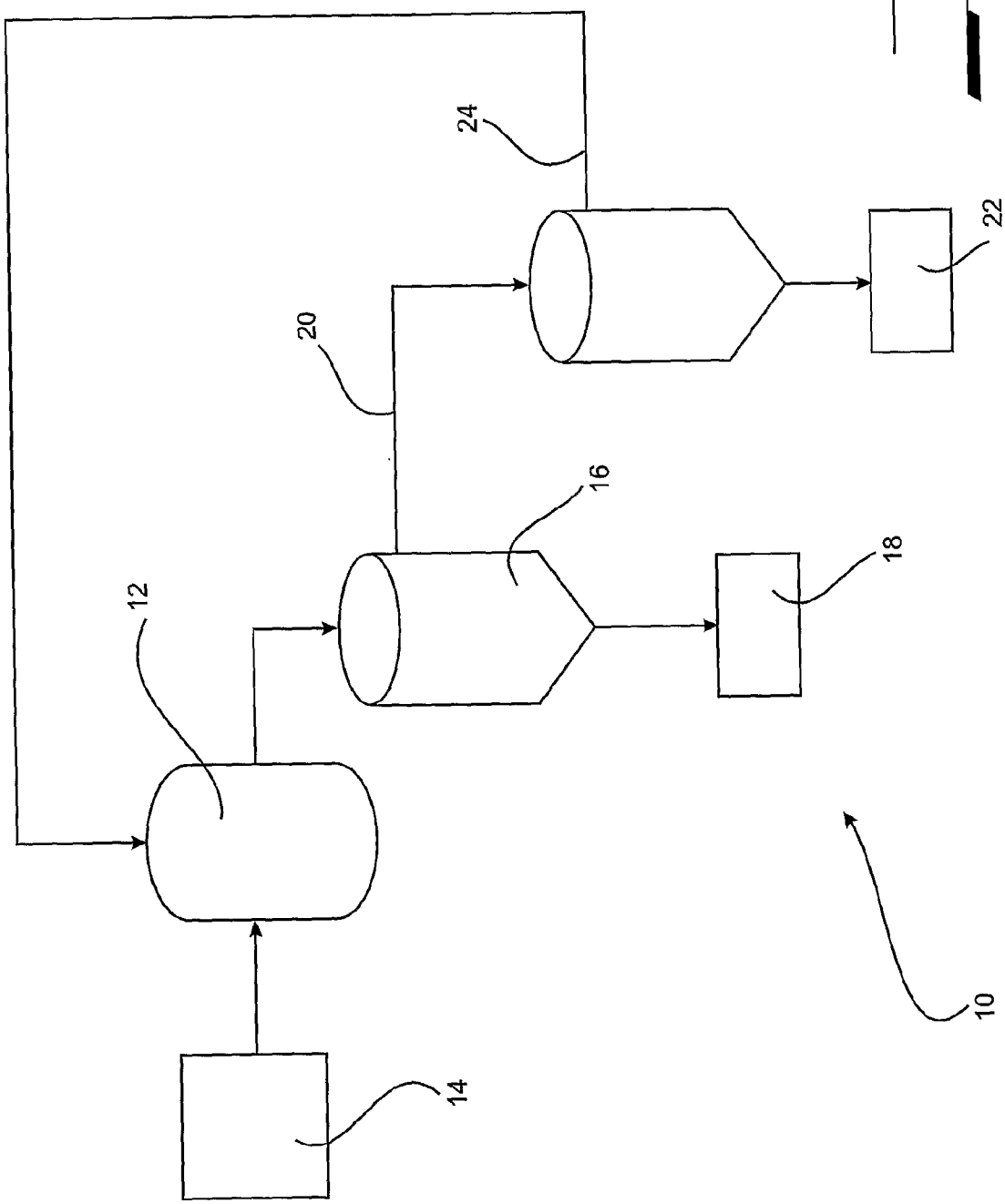


Fig 1a

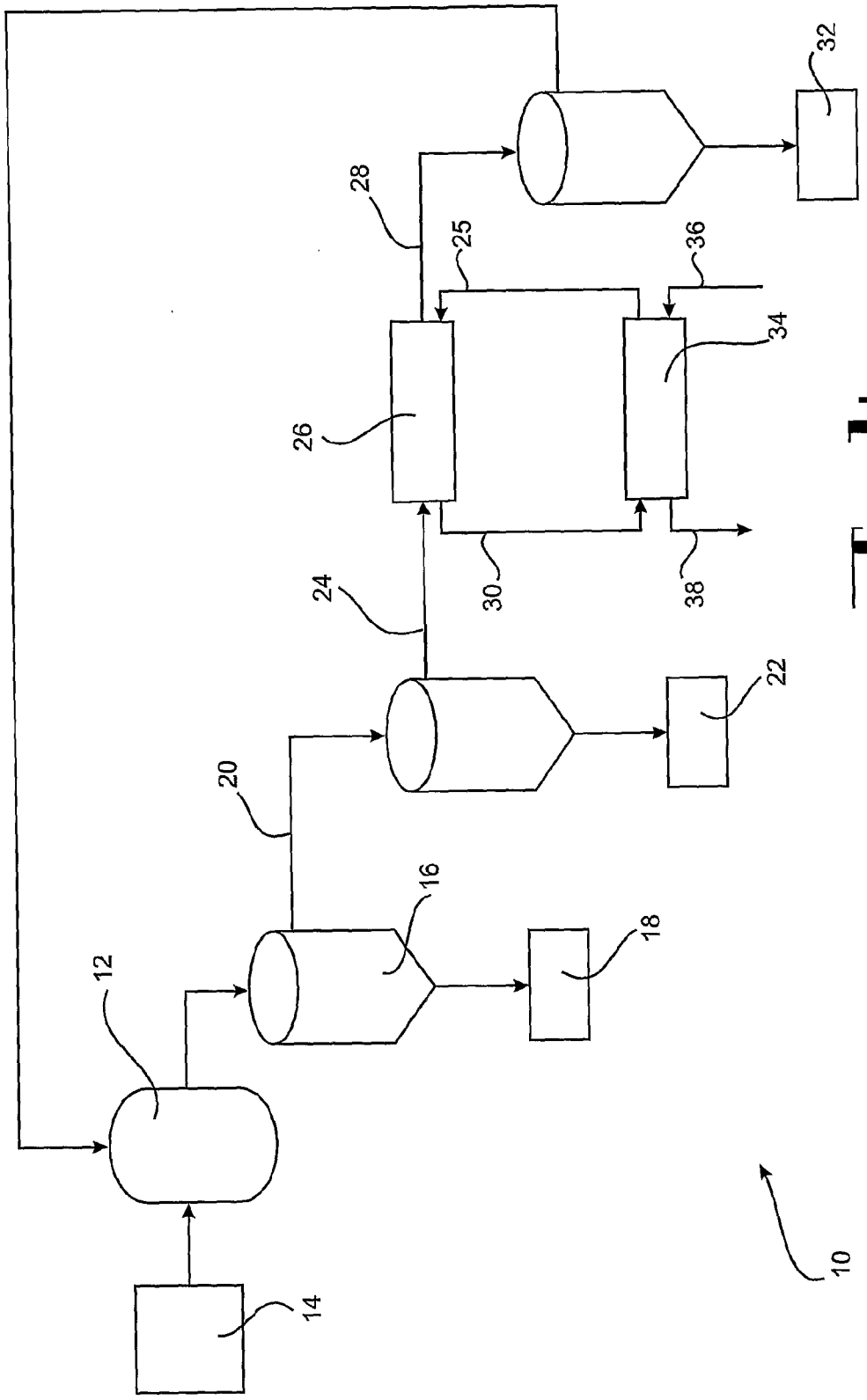


Fig. 1b

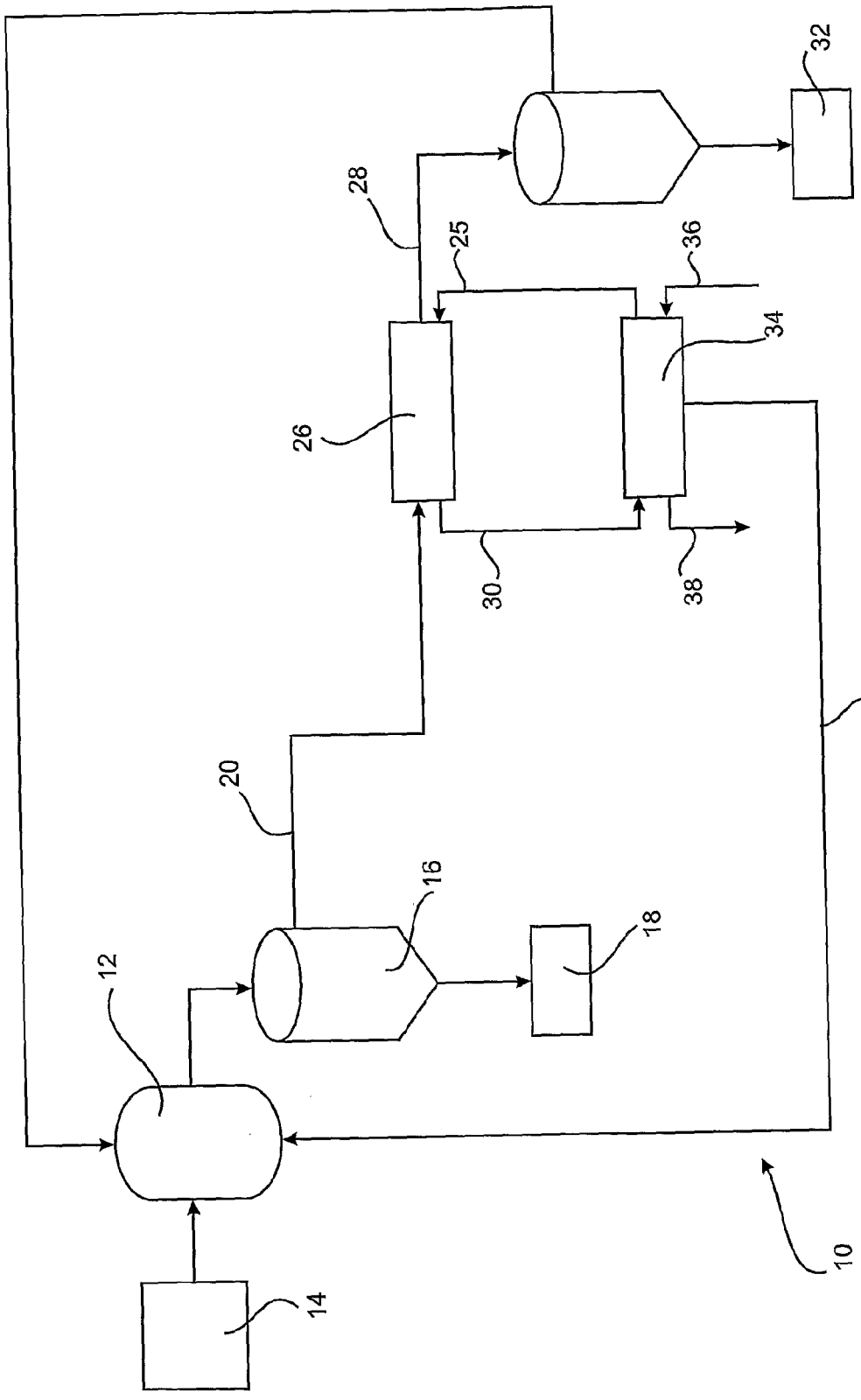


Fig. 1C

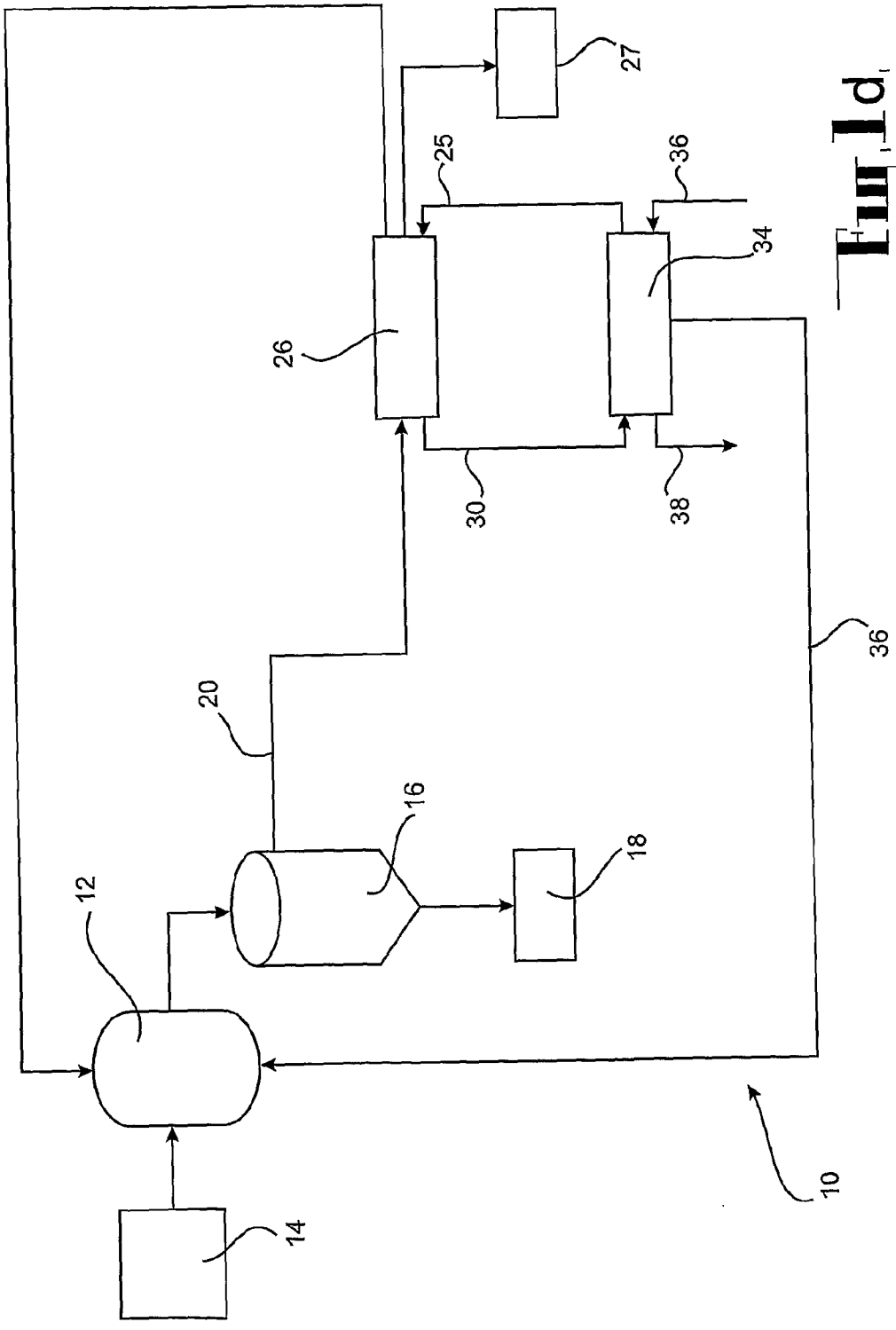


Fig. 1d

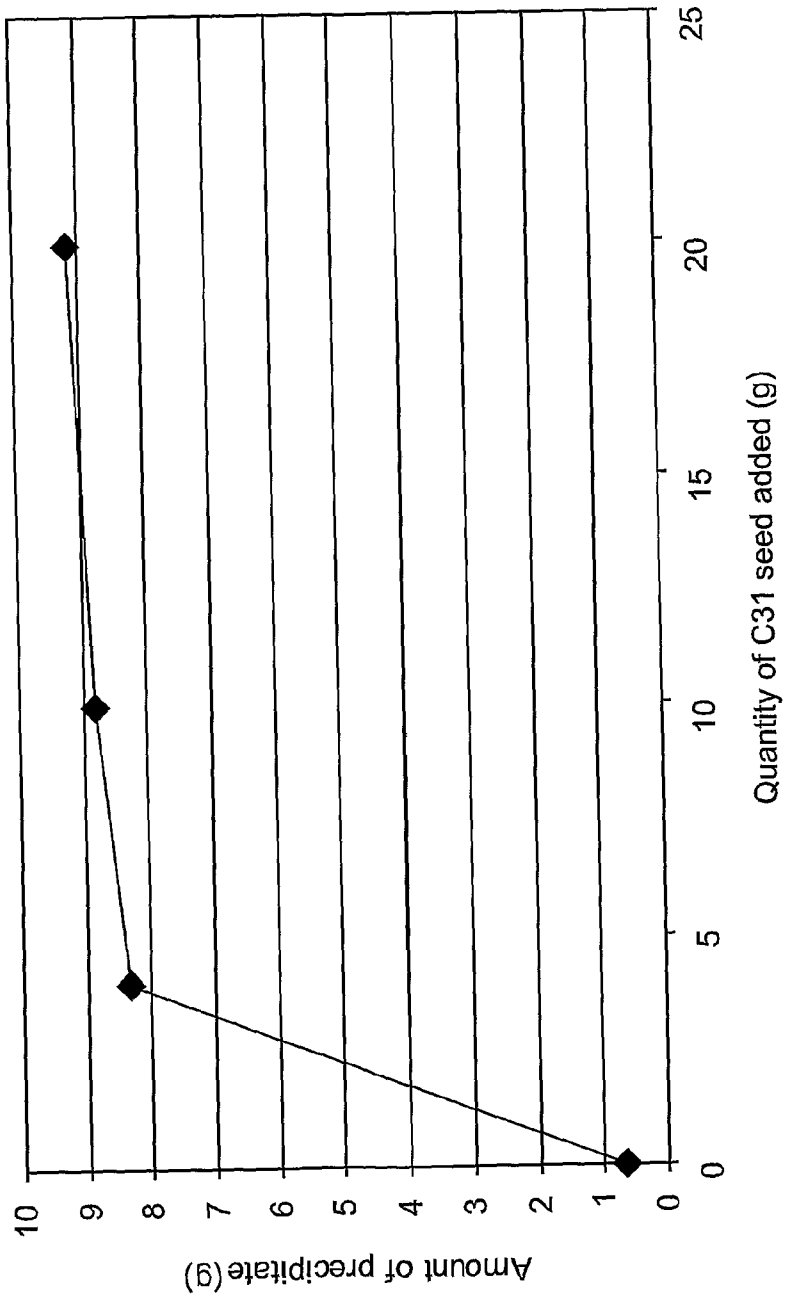

Amount of precipitate (g)
0
1
2
3
4
5
6
7
8
9
10
0
5
10
15
20
25
Quantity of C31 seed added (g)

Fig. 2

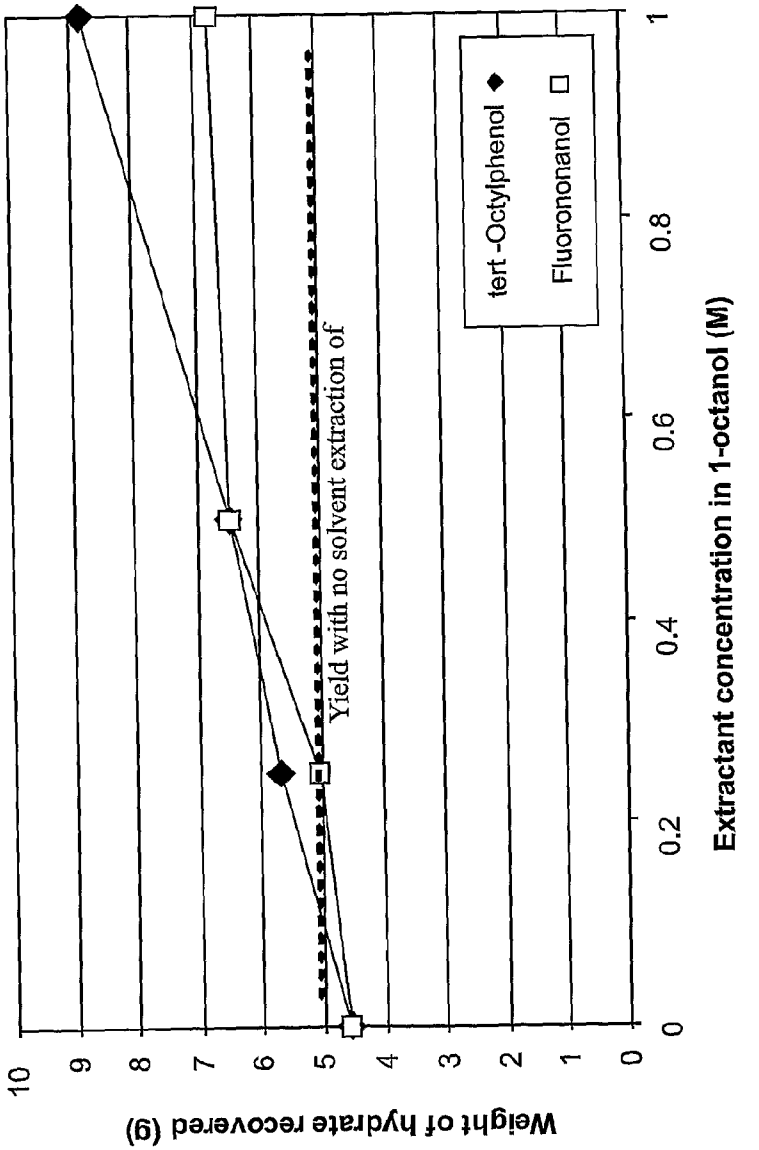

Weight of hydrate recovered (g)
10
9
8
7
6
5
4
3
2
1
0
0
0.2
0.4
0.6
0.8
1
Extractant concentration in 1-octanol (M)
tert -Octylphenol
Fluorononanol
Yield with no solvent extraction of

Fig. 3

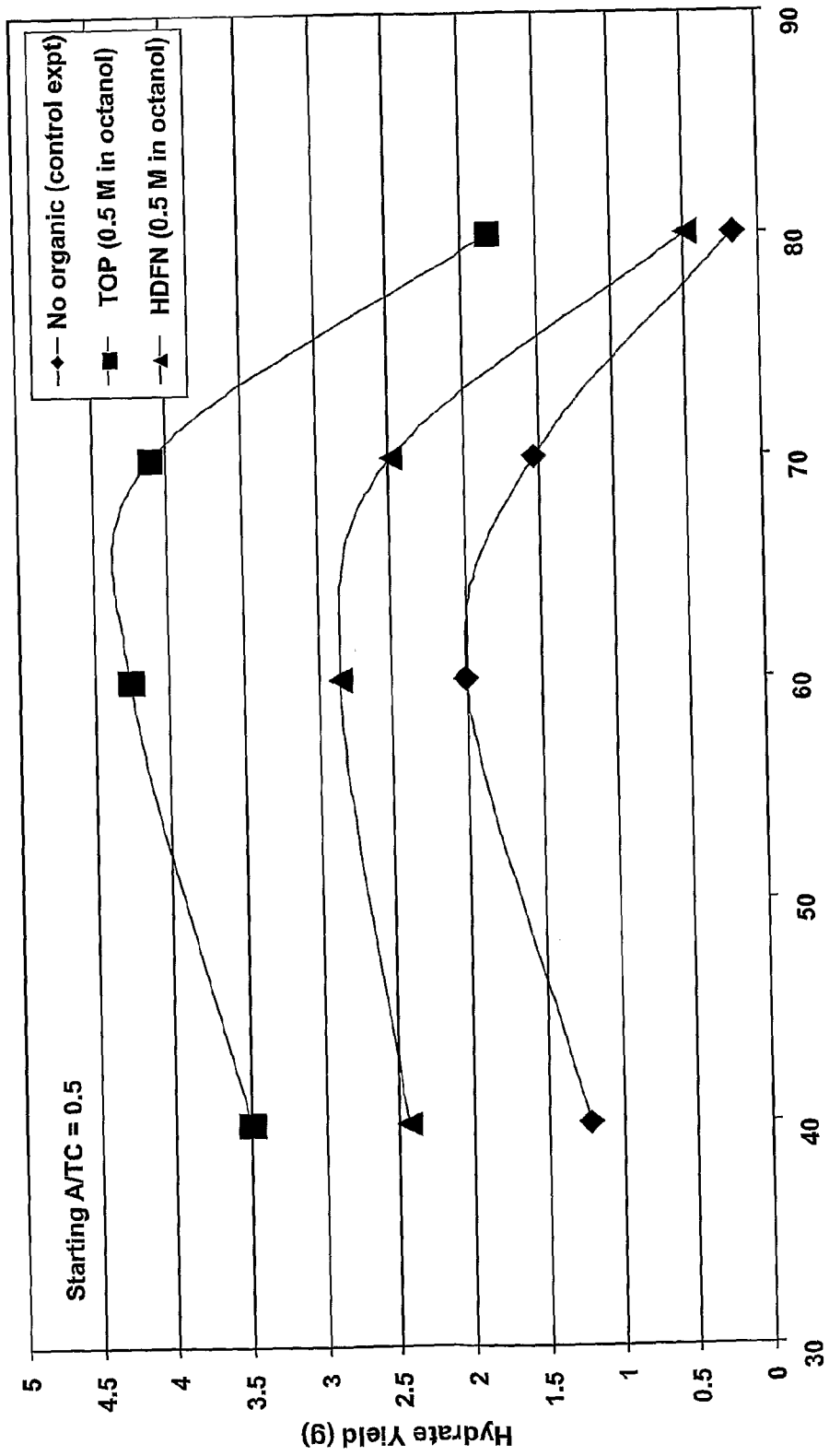

No organic (control expt)
TOP (0.5 M in octanol)
HDFN (0.5 M in octanol)
Starting A/TC = 0.5
Hydrate Yield (g)
Temperature (Celsius)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
30
40
50
60
70
80
90

Fig 4

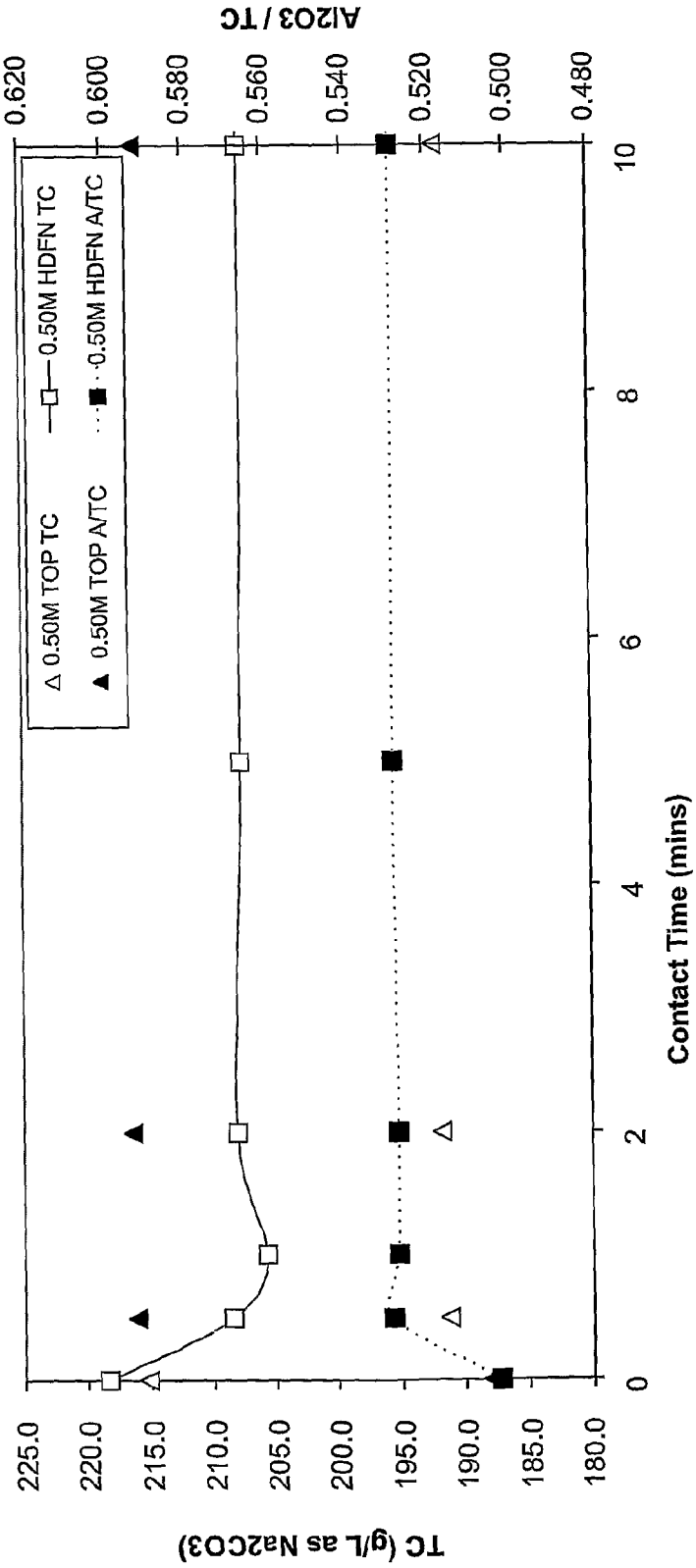

Al2O3 / TC
0.620
0.600
0.580
0.560
0.540
0.520
0.500
0.480
0.50M TOP TC
0.50M TOP A/TC
0.50M HDFN TC
0.50M HDFN A/TC
TC (g/L as Na2CO3)
225.0
220.0
215.0
210.0
205.0
200.0
195.0
190.0
185.0
180.0
0
2
4
6
8
10
Contact Time (mins)

Fig. 5

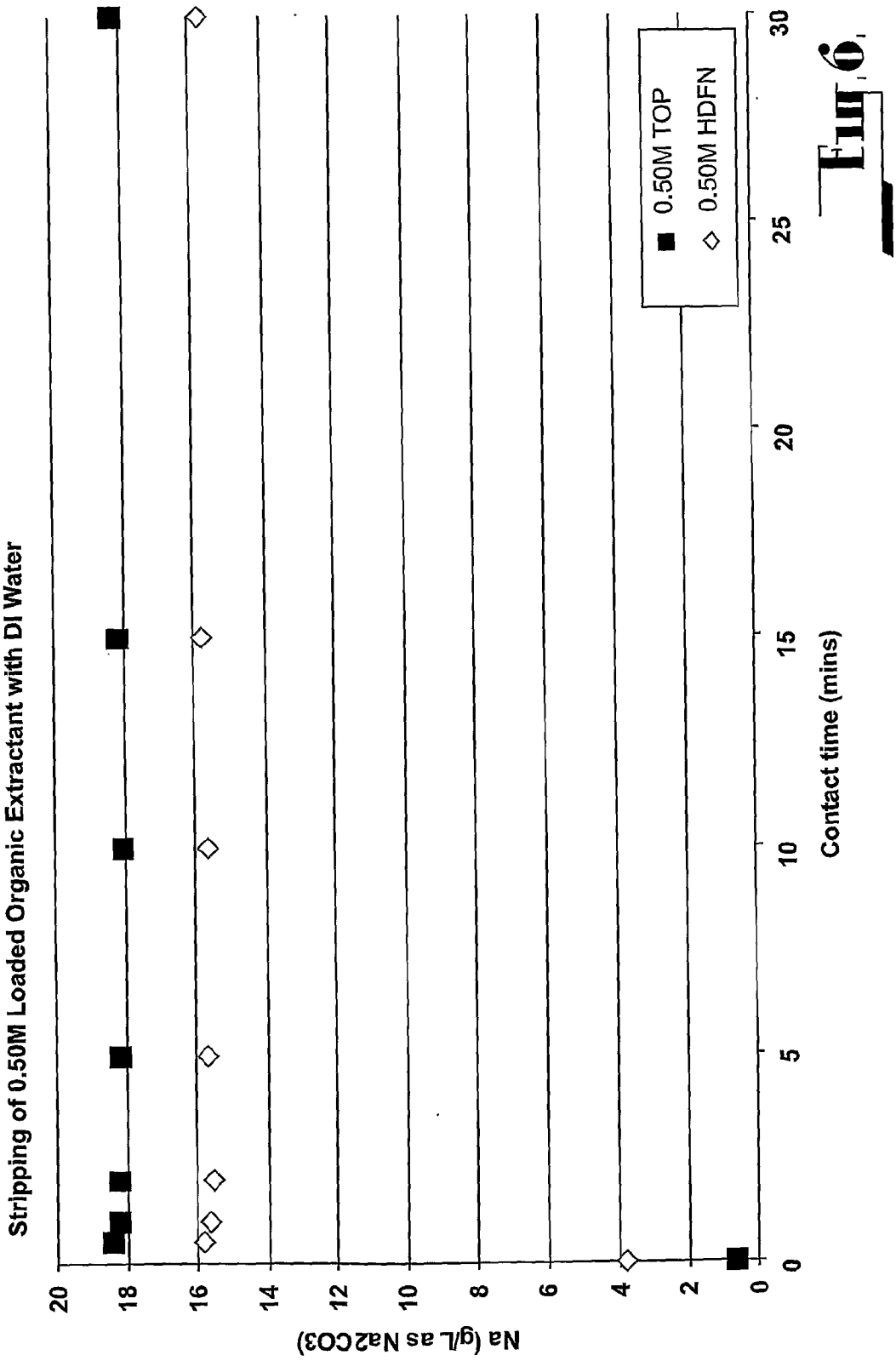

Stripping of 0.50M Loaded Organic Extractant with DI Water
Na (g/L as Na2CO3)
Contact time (mins)
0.50M TOP
0.50M HDFN
0
2
4
6
8
10
12
14
16
18
20
0
5
10
15
20
25
30

Fig 6

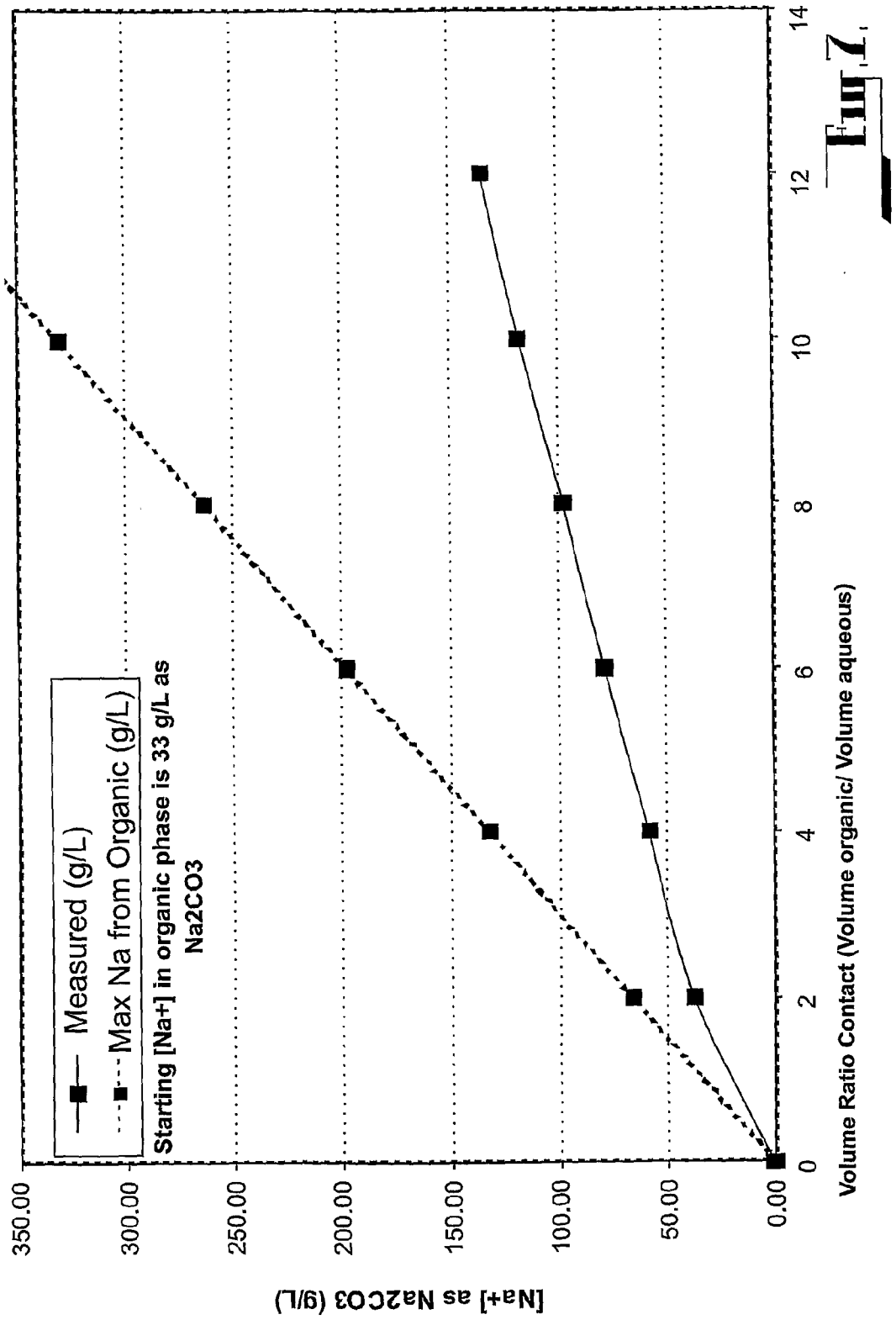

Measured (g/L)
Max Na from Organic (g/L)
Starting [Na+] in organic phase is 33 g/L as Na2CO3
[Na+] as Na2CO3 (g/L)
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
0
2
4
6
8
10
12
14
Volume Ratio Contact (Volume organic/ Volume aqueous)

Fig 1

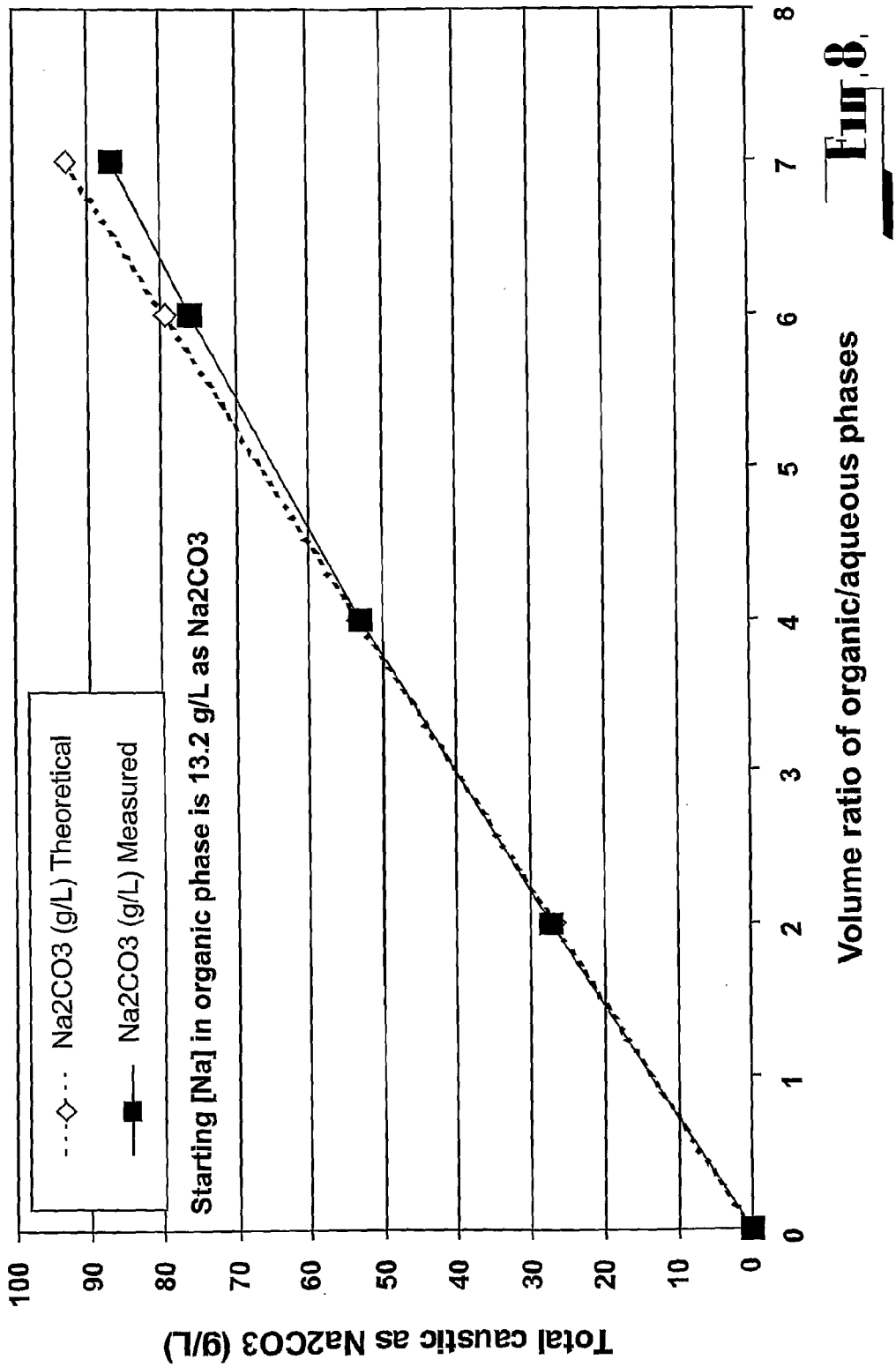

Total caustic as Na2CO3 (g/L)
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
Volume ratio of organic/aqueous phases
Starting [Na] in organic phase is 13.2 g/L as Na2CO3
Na2CO3 (g/L) Theoretical
Na2CO3 (g/L) Measured

Fig 8

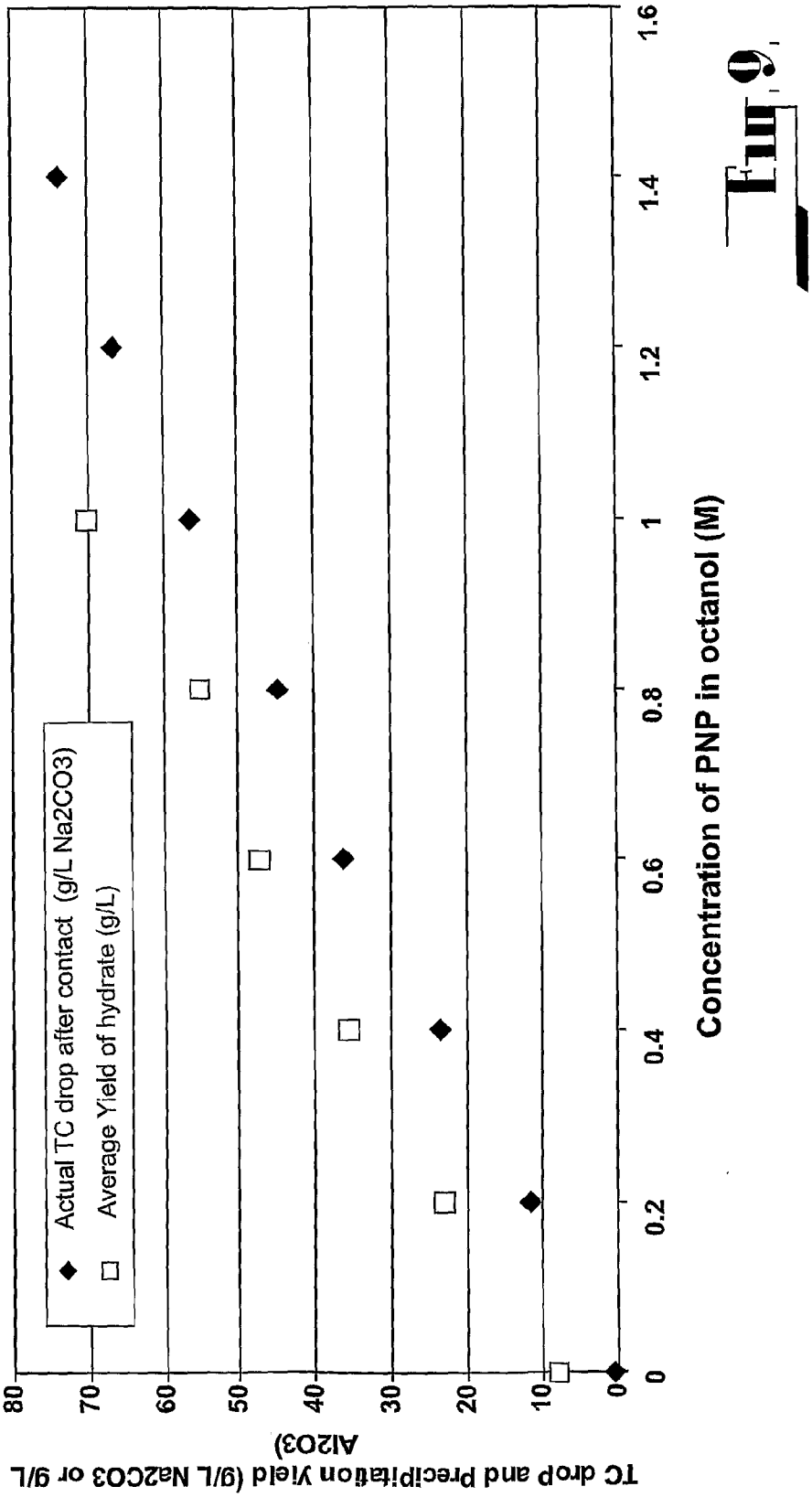

TC drop and Precipitation Yield (g/L Na2CO3 or g/L Al2O3)
Concentration of PNP in octanol (M)
Actual TC drop after contact (g/L Na2CO3)
Average Yield of hydrate (g/L)
0
10
20
30
40
50
60
70
80
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6

Fig. 9

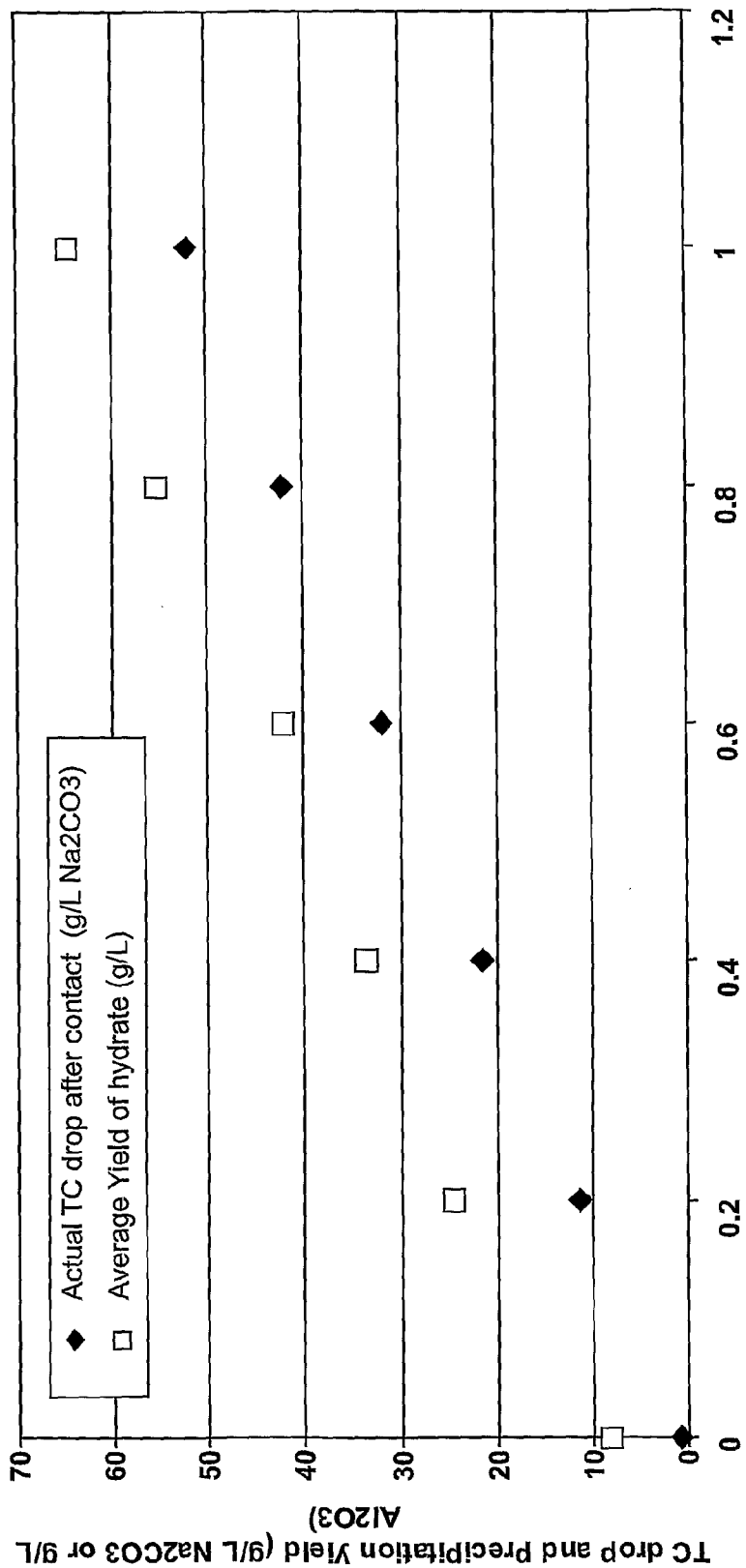

TC drop and Precipitation Yield (g/L Na2CO3 or g/L Al2O3)
Concentration of TOP in octanol (M)
Actual TC drop after contact (g/L Na2CO3)
Average Yield of hydrate (g/L)
0
10
20
30
40
50
60
70
0
0.2
0.4
0.6
0.8
1
1.2

Fig. 10

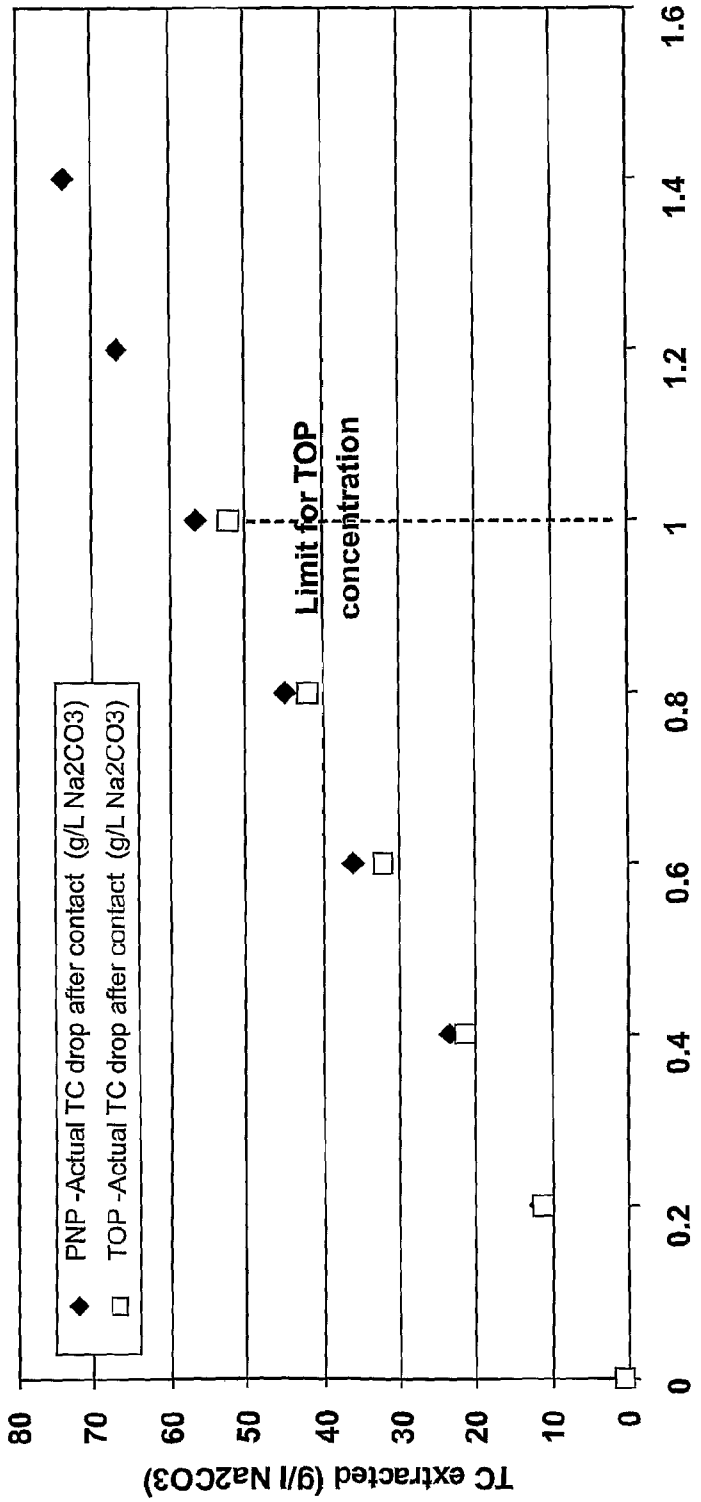

TC extracted (g/l Na2CO3)
0
10
20
30
40
50
60
70
80
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Concentration of extractant (M)
Limit for TOP concentration
PNP -Actual TC drop after contact (g/L Na2CO3)
TOP -Actual TC drop after contact (g/L Na2CO3)

Fig. 11

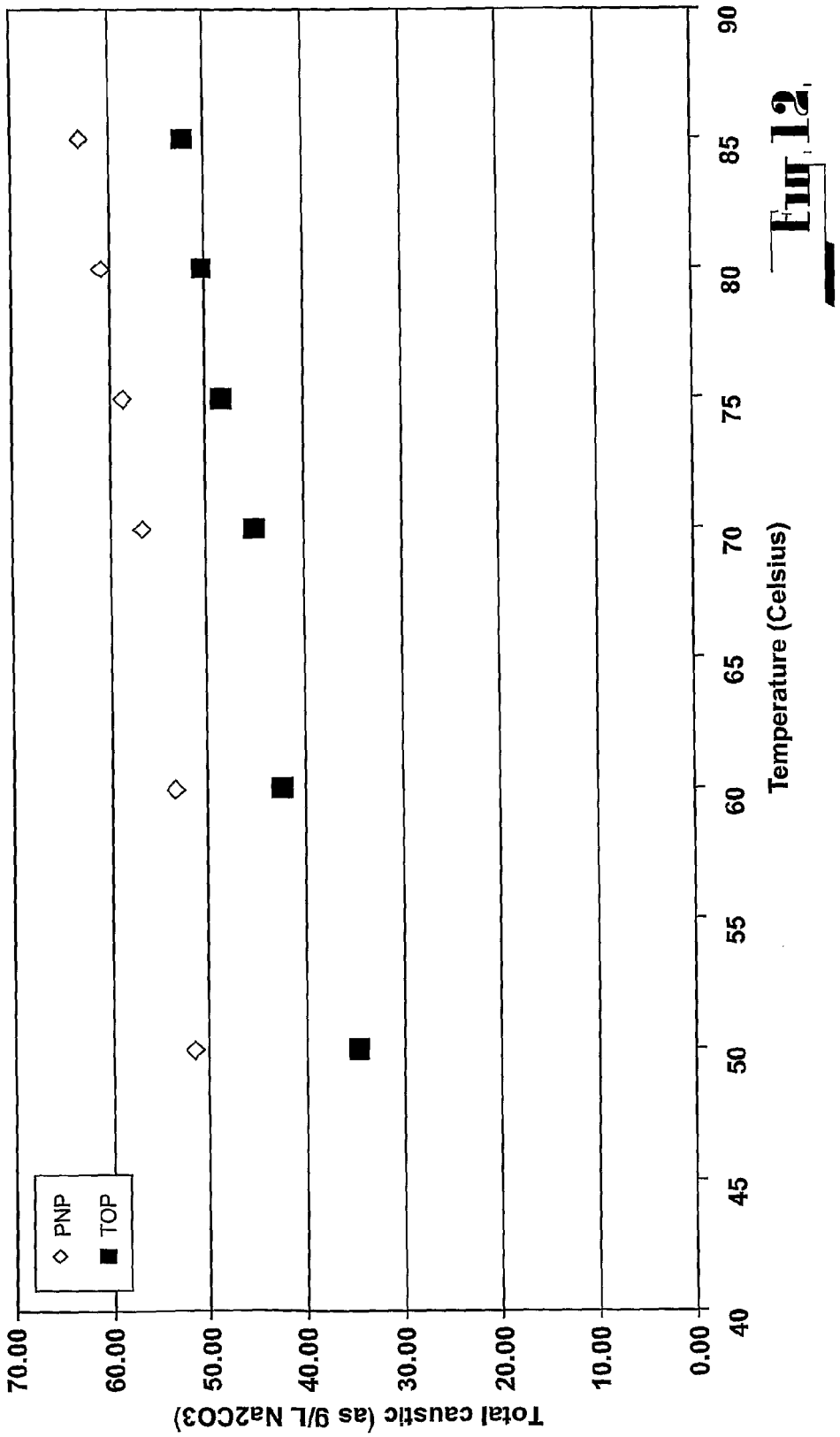

Total caustic (as g/L Na2CO3)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
40
45
50
55
60
65
70
75
80
85
90
Temperature (Celsius)
PNP
TOP

Fig 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2007/000426

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C01F 7/02 (2006.01) ***C01F 7/34*** (2006.01) ***C01F 7/47*** (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)
C01F 7/02, 7/34, 7/47

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)
WPAT; JAPIO; CAPLUS; USPTO; Espace@net; IPC (above) & keywords - Bayer+, alumin+, baux+, gibbsit+, cation+, sodium+, calcium+, soda+, extract+, remov+, separat+, precipitat+, impurit+, purif+, stripp+, (water immiscible solvent+), (weak acid+), (organic solvent+)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,Y	US 4581207 A (BUSH et al), 8 April 1986 Cols 4, 5 & 7	1-41
X,Y	US 3971843 A (HELGORSKY et al), 27 July 1976 Cols 2-4	1-41

[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
10 May 2007	17 MAY 2007
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. (02) 6285 3929	Authorized officer **WARREN TAYLOR** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : (02) 6283 2229

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2007/000426

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,Y	US 4485076 A (BAUER et al), 27 November 1984 Cols 1, 4-5	1-41
X,Y	US 4559203 A (BAUER et al), 17 December 1985 Cols 3-4, Example 1	1-41
X,Y	US 4724129 A (HELGORSKY et al), 9 February 1988 Whole document	1-41
X,Y	EP 0143749 A (GEBRUDER SULZER AG), 5 June 1985 Whole document	1-41
D,Y	US 6322702 B1 (MOYER et al), 27 November 2001 Cols 1-7, claim 15	1-41

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU2007/000426

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					
US	4581207	US	4464347				
US	3971843	AU	82911/75	CA	1052582	CH	602220
		DE	2530880	ES	439330	FR	2277897
		FR	2307047	FR	2307882	GB	1513398
		JP	51032411	YU	175375		
US	4485076	AU	18354/83	BR	8304593	CA	1203386
		EP	0102280	ES	8500869	FR	2532295
		JP	59092914	NZ	205367		
US	4559203	AU	18353/83	BR	8304594	CA	1233645
		EP	0102882	ES	8500870	FR	2532296
		JP	59092915	NZ	205366		
US	4724129	AU	29097/77	CA	1099522	CH	610931
		DE	2743475	ES	462677	FR	2365641
		GB	1593289	GR	61676	JP	53052289
		YU	227677				
EP	0143749	AU	36135/84	BR	8405943	CH	656643
		NO	852826	WO	8502390		
US	6322702						

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

END OF ANNEX