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Matjie et al. (43) **Pub. Date: Nov. 4, 2004**(54) **SELECTIVE RECOVERY OF ALUMINIUM,
COBALT AND PLATINUM VALUES FROM A
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Publication Classification(51) **Int. Cl.⁷** **C22B 11/00**(52) **U.S. Cl.** **423/22**(57) **ABSTRACT**

The invention provides a process for the selective recovery of aluminium, cobalt and platinum, and compounds thereof, from a catalyst composition including aluminium, cobalt and platinum, said process including the steps of treating the catalyst composition to selectively get ions of substantially only one of the aluminium, cobalt and platinum into solution, recovering, in separate process steps, the thus treated aluminium, cobalt, or platinum in salt or metal form, and repeating the treating and recovering steps for each of the aluminium, cobalt and platinum. The treating steps may include process steps such as leaching, washing, dissolving, stripping, and the like. The recovery steps may include filtration, precipitation, separation, flocculation, and the like.

SELECTIVE RECOVERY OF ALUMINIUM, COBALT AND PLATINUM VALUES FROM A SPENT CATALYST COMPOSITION

FIELD OF THE INVENTION

[0001] This invention relates to the selective recovery of metal values from a spent catalyst composition. In particular this invention relates to a process for the selective recovery of aluminium, Cobalt and Platinum and/or compounds thereof, from a spent catalyst composition.

BACKGROUND TO THE INVENTION

[0002] The specific spent catalyst composition of the current invention is obtained from Fischer Tropsch synthesis reactions for the production of predominantly paraffinic hydrocarbons.

[0003] The catalyst is an impregnated Fischer Tropsch Catalyst comprising an alumina carrier and active component selected from the group consisting of cobalt and/or iron and mixtures thereof. The catalyst may also comprise of a group VIII noble metal as promoter.

[0004] The Fischer-Tropsch process is used to produce hydrocarbons from carbon monoxide and hydrogen. In the Fischer-Tropsch process, a cobalt catalyst may be used to activate the catalytic reaction. This catalyst may be prepared with a cobalt nitrate and tetra amine platinum nitrate that are used as cobalt and platinum precursors respectively. Aluminium oxide may be used as a support. Continual processing causes a drop in the activity of the catalyst mainly due to sulphur, which is originally present in the mixture of gases, which may accumulate on the surface of the catalyst to form either cobalt sulphide or platinum sulphide during the process. Coke formation may also be experienced during the process and subsequently the catalyst reaches a stage of deactivation and becomes a spent catalyst.

[0005] The spent catalyst typically contains organic material, cobalt oxide, platinum and aluminium oxide. As a result of the organic content in the catalyst coupled with the fact that both cobalt and platinum are considered to be environmentally toxic, dumping is not a viable option. If the adequate disposal of this spent catalyst, which is oily and sticky, is considered, the chemical fixation method should be recommended. In this method, which is very expensive, the pollutants like heavy and base metals can react with cement or pozzolanic materials to form water insoluble compounds. This encapsulation of heavy and base metals on the spent catalyst is efficacious only if the heavy metals are not absolutely leached out in the soil by water. To avoid the disposal of the spent catalyst or encapsulated deactivated catalyst in the landfills, the recovery of these high value metals is important.

[0006] The inventor is aware that the above catalyst composition contains valuable metal values which, if recovered, could lead to a substantial profit and also to eliminate the existing environmental problems. At present the catalyst composition is disposed of without substantial recovery thereof.

SUMMARY OF THE INVENTION

[0007] To produce environmentally friendly products from the spent catalyst, a method of recovering high value

metal compounds from the spent cobalt based catalyst which is environmentally safe, has been developed.

[0008] In this selective recovery process initially either the mixture of spent catalyst and sodium carbonate or the spent catalyst containing organic material is calcined at different temperatures in the presence of air to oxidise the organic material. Following the calcination of this spent catalyst, metal oxides such as cobalt oxide (CoO and Co_3O_4), cobalt aluminate (Co_2AlO_4) and sodium aluminate ($\text{Na}_2\text{Al}_2\text{O}_4$) are formed. A solution of caustic soda (sodium hydroxide) is used to selectively and efficiently dissolve aluminium oxide at a relatively high temperatures (ranging from 110 to 220 Degrees Celsius) and pressures (ranging from 5 to 20 bars) with substantially no dissolution of cobalt and platinum from the spent catalyst. The pH of the mixture is around 13.

[0009] Alternatively, water leaching may be used to solubilise sodium aluminate formed during the calcination step. This sodium aluminate solution which is formed during the leaching step may be used in the precipitation step of the aluminium hydroxide. The cobalt and platinum, which are theoretically insoluble in a solution of sodium hydroxide under afore-given conditions, remain in the leached residue after the base leaching. This leached residue containing mainly platinum and cobalt are dissolved in a solution of nitric acid to form cobalt nitrate while the platinum remains in the acid-residue after the acid leaching step.

[0010] This acid residue may be dissolved in the aqua regia (a solution of nitric acid and hydrochloric acid) to form chloroplatinic acid.

[0011] Subsequently, purification methods such as solvent extraction and selective precipitation may be used to selectively remove impurities or the desired metal ions from the leach liquors of the basic residue and acidic residue. The purified leach liquors may be reserved for the crystallisation method. In this method, chemically pure crystalline cobalt nitrate or diammonium hexachloroplatinate are formed.

[0012] The platinum salts are important in the purification of platinum metal and sponge while the cobalt nitrate is commercially used in the production of high purity cobalt, in the electronics and chemical industries.

[0013] Thus, according to a first aspect of the invention, there is provided a process for the selective recovery of aluminium, cobalt and platinum, and compounds thereof, from a catalyst composition including aluminium, cobalt and platinum, said process including the steps of:

[0014] treating the catalyst composition to selectively get ions of substantially only one of the aluminium, cobalt and platinum into solution;

[0015] recovering, in separate process steps, the thus treated aluminium, cobalt, or platinum in salt or metal form; and

[0016] repeating the treating and recovering steps for each of the aluminium, cobalt and platinum.

[0017] The treating steps may include process steps such as leaching, washing, dissolving, stripping, and the like.

[0018] The recovery steps may include filtration, precipitation, separation, flocculation, and the like.

[0019] Thus, according to a second aspect of the invention, there is provided a process for the selective recovery of aluminium, cobalt and platinum, and compounds thereof, from a catalyst composition including aluminium, cobalt and platinum, said process including the steps of:

[0020] oxidising substantially all organic material present with the catalyst composition;

[0021] leaching the aluminium and/or compounds thereof from the oxidised catalyst composition with a strong or weak base to form an aluminium containing product and a filtrate;

[0022] filtering of alkali insoluble residue from the filtrate;

[0023] washing of the alkali insoluble residue with water to remove the residual alkali aluminate solution;

[0024] precipitating of silica from alkali aluminate with slaked lime or quicklime;

[0025] filtering of insoluble silicate from alkali aluminate;

[0026] crystallising aluminium trihydrate from the alkali aluminate solution;

[0027] filtering aluminium trihydrate crystals from the alkali aluminate solution

[0028] recycling of the alkali solution to the leaching step;

[0029] dissolving the cobalt and compounds thereof present in the water washed-insoluble residue composition with an inorganic acid;

[0030] separating a substantial portion of the cobalt rich solution from a solid component present after the dissolving step;

[0031] precipitating substantially all non-cobalt and/or non-cobalt compound impurities from the cobalt rich solution;

[0032] crystallizing the cobalt and/or cobalt compounds out of the cobalt rich solution to form impure cobalt nitrate salt; or

[0033] as an alternative to the crystallizing step, selectively loading substantially all cobalt ions from the impure cobalt rich solution into an organic phase by solvent extraction;

[0034] subsequently stripping the cobalt-containing organic phase with a solution of nitric acid to form a pure cobalt nitrate salt;

[0035] dissolving the platinum and compounds thereof, as well as non-cobalt and/or non-cobalt compound impurities from the cobalt rich solution out of the water washed solid component to obtain a platinum rich solution; and

[0036] recovering platinum and/or platinum salts from the platinum rich solution.

[0037] After the aluminium leaching step and prior the alkali insoluble residue filtration step a flocculation step may be included to remove ultra fine solids which inhibit efficient filtration.

[0038] Also, after the cobalt dissolution step and prior to the separation of a substantial portion of the cobalt rich solution a flocculation step may be included to remove ultra fine solids which may inhibit efficient separation.

[0039] The flocculation for an alkali slurry may be carried out with the aid of flocculating agents, such as modified anionic polyacrylamides. The flocculation may be carried out at a pH of about 12. The flocculation may assist the sedimentation rate and filterability of suspended ultra fine solid particles from the slurry

[0040] The flocculation for an acidic slurry may be carried out with the aid of flocculating agents such as cationic a flocculant. The flocculation may carried out at a low pH about 1.5. The flocculation may assist the sedimentation rate and filterability of suspended ultra fine solid particles from the slurry.

[0041] The catalyst composition may be in the form of waxy lumps of spent catalyst composition from a hydrocarbon processing reactor.

[0042] The oxidising step may be performed by heating the catalyst composition and contacting it with oxygen.

[0043] Typically, for performing the oxidising step, the catalyst composition is heated to a temperature of between 600° C. and 1400° C., generally between 700° C. and 1000° C. In specific embodiments of the invention the catalyst composition was heated to 700° C., 800° C., 900° C. and 1000° C.

[0044] Where the catalyst composition is Co/Pt/Al₂O₃/SiO₂, then the oxidised spent catalyst composition typically contains about from 0.0125 g Pt per 100 g Al₂O₃ to 0.175 g Pt per 100 g Al₂O₃ and from 5 g Co per 100 g Al₂O₃ to 70 g Co per 100 g Al₂O₃.

[0045] The leaching of the aluminium and/or the aluminium compounds, such as Al₂O₃, from the oxidised spent catalyst composition may be carried out with a solution of sodium hydroxide of about 20% to 50% w/w NaOH, typically 25%. This selectively and efficiently dissolves aluminium oxide at a relatively high temperature ranging from 110° C. to 250° C., typically 200° C., and at a high pressure ranging from 5 to 20 bar, typically 15 bar, with substantially no dissolution of cobalt and platinum from the spent catalyst composition. The leachate may be in the form of slurry.

[0046] The flocculation of the slurry prior to filtration may be carried out using approximately 2% w/w of flocculant prepared using a solution of sodium hydroxide of about 2% w/w NaOH, whereafter the flocculant solution is conditioned at ambient temperature for one hour to form homogeneous solution, whereafter it is diluted with a solution of sodium hydroxide of 2% w/w NaOH to produce a final solution containing about 0.25% w/w of the flocculant.

[0047] Approximately 3000 to 6000 g/t of the final solution heated to 90 degrees Celsius may be added to the slurry and mixed thoroughly until flocs form. These flocs may be separated from the mixture by filtration and eventually washed with water to remove aluminium-containing filtrate absorbed during the filtration.

[0048] Alternatively, water leaching could also be used to selectively solubilize sodium aluminate formed during the oxidising of the spent catalyst in the presence of either

sodium carbonate or sodium chloride. The water leaching may be carried out at any temperature and pressure, and 50° C. at atmospheric pressure has been found to be satisfactory. A solution of sodium aluminate from the water leaching step may be reserved for the precipitation of aluminium hydroxide while the water-washed base insoluble residue may be used in the strong or weak inorganic acid cobalt dissolving step.

[0049] The leached residue recovered from the aluminium leaching step typically contains 51% w/w cobalt, 0.124% w/w platinum and 4.9% w/w aluminium.

[0050] Cobalt and platinum are currently considered to be environmentally toxic and thus dumping of this leached residue is not a viable option. Also, both cobalt and platinum are high value products.

[0051] Cobalt recovery is initiated by dissolving the cobalt and compounds thereof present in the water-washed leached residue of the oxidised catalyst composition with a strong acid such as nitric acid. The water washed-leached residue may be contacted with a solution of nitric acid of about 55% w/v HNO_3 at a temperature of between 80° C. and 200° C. and at a pressure of between 1 bar and 20 bar, in order to selectively dissolve cobalt. Typically this cobalt dissolution step is carried out at 100° and 1 atmospheric pressure.

[0052] The impure cobalt nitrate may be used in the chemical, ceramics Industries and the production of high purity cobalt for use in the electronics and related industries. The washed nitric acid insoluble residue, which is mainly composed of platinum compounds and impurities, may be used in the step of producing platinum compound.

[0053] In order to recover commercially viable cobalt, the process includes the separating of a substantial portion of the impure cobalt nitrate, i.e. the cobalt rich solution, from the strong acid insoluble residue, i.e. the solid component present after the dissolving step. This separation may include a precipitation step during which impurities such as Aluminium and Iron are precipitated out of the cobalt rich solution.

[0054] The separation may be aided by flocculating ultra fine solids using a suitable flocculant, such as ZN92V Zetafloc produced by Zetachem Company. The flocculant may be used as 0.1% w/w solution.

[0055] The still impure cobalt rich solution is then purified by selectively removing substantially all only cobalt ions from the cobalt rich solution by solvent extraction. The impurities may remain in the aqueous phase after the solvent extraction step.

[0056] The cobalt rich solution from the precipitation step typically contains Co, Pt, Al, Fe, NO_3^- and NH_4^+ ions. To selectively separate Co ions from this solution, a suitable type of an acidic extractant like di-(2ethylhexyl) phosphoric acid (DEHPA) and tributylphosphate (TBP) as a modifier in illuminating paraffin for extracting Co ions from the cobalt rich solution may be used. Usually this solvent extractant is used as an ammonium salt which assists in keeping the pH of the mixture relatively constant after contacting the acidic cobalt rich solution with the organic extractant phase.

[0057] The aqueous phase recovered from the solvent extraction may be used in the precipitation of Fe and Al ions

step, while the loaded organic phase (containing mainly Co ions) is reserved for a stripping step.

[0058] In this step, the Co loaded organic phase is contacted with a solution of the stripping agent, such as a solution of nitric acid, to remove the extracted species i.e. Co ions.

[0059] The purified cobalt rich solution is finally crystallised to form a red-brown crystalline cobalt nitrate salt, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ depending on the retention time when heating the crystals at 55° C.

[0060] This salt is currently used in the production of high purity cobalt and also electronics and chemical industries.

[0061] The crystallisation liquor containing free water and nitric acid may be utilised in the crystallisation step of cobalt nitrate or in the dissolution step of cobalt from the washed insoluble basic residue.

[0062] Platinum is recovered from the nitric acid insoluble solid component from the cobalt dissolution step by dissolving the platinum and compounds thereof, as well as non-cobalt and/or non-cobalt compound impurities from the cobalt rich solution out of the solid component to obtain a platinum rich solution. The dissolving of platinum may be achieved by a mixture of HCl and HNO_3 or by using H_2O_2 and HCl or HCl and Cl_2 .

[0063] The dissolved platinum may be precipitated out of the platinum rich solution by using NaOH and/or NH_4Cl to form platinum salts complex which can be recovered by a liquid: solid separation process such as filtration.

[0064] The recovered aluminium, cobalt and platinum, and/or compounds or salts thereof may be further processed.

SPECIFIC DESCRIPTION AND EXAMPLES

[0065] The invention will now be described with reference to the following examples, which are not intended to limit the scope of the invention.

1. Oxidising of the Spent Catalyst Composition—Oxidising Step

[0066] The spent catalyst composition from a Fischer-Tropsch reaction for the industrial synthesis of certain hydrocarbons from carbon monoxide and hydrogen typically contains about 60 to 75% of the organic content.

[0067] This spent catalyst is initially heated to a temperature ranging from 700 to 1000° C. at atmospheric pressure for 2 to 6 hr in the presence of air to oxidise the organic material. A high temperature furnace (maximum temperature of the furnace is 1400° C. was used for the heating.

[0068] In another run, the spent catalyst composition was oxidised in the presence of either sodium carbonate or sodium chloride to prevent the formation of the spinels such as cobalt aluminate (Co_2AlO_4) and cobalt (II) dicobalt (III) oxide (Co_3O_4) during the oxidising step. The aluminium oxide or cobalt oxide that is present in the spinels may possibly dissolve with difficulty in a solution of sodium hydroxide or mineral acid solution. During the oxidising step, sodium oxide from either sodium carbonate or sodium chloride could possibly react with water-insoluble aluminium oxide to form water-soluble compounds such as sodium aluminate or silicate.

[0069] The oxidised spent catalyst composition sample produced in this step is digested with either water or a weak solution of sodium hydroxide (approximately 10 to 25% w/w NaOH) at a relatively high temperature ranging from 90 to 230° C. and at high pressure ranging from 1 to 20 bars.

[0070] The main objective of the oxidising step is to burn out almost all of the organic material present in the spent catalyst composition prior to the leaching step as this organic material can decompose the lixiviant reagents during the leaching step.

[0071] a. Experimental Procedure

[0072] Approximately 1000 g of the waxy lumps of the spent catalyst composition was placed in a stainless steel dish. A gas burner was used to ignite the waxy lumps in the presence of air. A self-supporting combustion of the waxy lumps of the spent catalyst composition under natural convection was carried out for two hours and no more combustion takes place. To oxidise all of the organic material remaining in the oxidised spent catalyst composition, a sample of a free flowing powder was oxidised at different temperatures ranging from 600 to 1000° C. for six hours in the presence of air.

[0073] A second sample of free flowing powder and sodium carbonate or sodium chloride were mixed together using solid to solid ratio of 1:1 (a sample of flowing powder: either sodium carbonate or sodium chloride) and finally, reoxidised under the above conditions. Subsequently, a sample of free flowing powder produced after a self-supporting combustion and a sample after oxidising the spent catalyst at various temperatures were submitted for the organic carbon analysis.

[0074] b. Results and Discussion

[0075] Visual observation showed that no significant catalyst dust loss was experienced during the oxidising. After the oxidising step, a free flowing powder with a small amount of residual carbon was produced. Following the oxidising of the spent catalyst at 1000° C. in the absence of both sodium carbonate and sodium chloride the colour of the oxidised spent catalyst composition turned to blue. This may possibly be attributed to the formation of cobalt aluminate at a high temperature. While after oxidising the spent catalyst composition at a temperature ranging from 700 to 1000° C. in the presence of sodium carbonate or sodium chloride, the colour of the oxidised spent catalyst composition turned black. This may mean that sodium aluminate was formed.

[0076] The loss on ignition (L.O.I) analysis of a free flowing powder formed during self-supporting combustion was determined to be 2.7%. This implies that the organic material was still contained in the free flowing powder after the self-supporting combustion. After reoxidising the free flowing powder for a period of six hours, the L.O.I of the final oxidised spent catalyst was determined to be <0.1. This implies that all of the residual carbon was effectively removed after the second oxidising step.

[0077] It can be concluded that all of the organic material present in the waxy lumps of the spent catalyst composition was successfully oxidised after the oxidising step. Spinels such as cobalt aluminate and cobalt(II) dicobalt (III) oxide were formed at high temperatures ranging from 900 to 1000° C. during the heating of the spent catalyst in the absence of either sodium carbonate or sodium chloride.

2. Leaching of the Oxidised Spent Catalyst Composition—Base Leaching Step

[0078] The oxidised spent catalyst from the waxy lumps of the spent catalyst composition typically contains about 60 to 65% Al_2O_3 , 18.7 to 19.6% w/w Co and 0.046 to 0.05% w/w Pt. A solution of sodium hydroxide of about 20 to 50% w/w NaOH was used to selectively and efficiently dissolve aluminium oxide at relatively high temperatures ranging from 110 to 170° C. and at high pressures ranging from 5 to 20 bars with substantially no dissolution of cobalt and platinum from the spent catalyst.

[0079] In a separate run, water leaching was used to selectively solubilize sodium aluminate formed during the calcination of the spent catalyst in the presence of either sodium carbonate or sodium chloride.

[0080] A solution of sodium aluminate from the leaching step was reserved for the precipitation of aluminium hydroxide while the water-washed base insoluble residue was used in the nitric acid leaching step.

[0081] a. Experimental Procedure

[0082] Approximately 420 g of the oxidised spent catalyst composition was placed in a 2500 ml Teflon vessel containing about 1260 g of either 25% w/w NaOH (a separate run was carried out with 50% w/w NaOH). This slurry was heated to 170° C. in a high pressure autoclave for 4 hr. The pressure of the slurry was increased to 9 bars (gauge pressure).

[0083] The spent catalyst sample which was oxidised in the presence of either sodium carbonate or sodium chloride was digested with water at 90° C. at atmospheric pressure to remove water soluble sodium aluminate.

[0084] After the leaching step, the sodium hydroxide-insoluble residue was separated from the leach liquor by normal filtration and washed thoroughly with enough water to remove the residual leach liquor from the filtercake. To further improve the aluminium extraction efficiency, two steps of leaching were used. In these two steps of leaching, the filtercake from the first leaching step was contacted with a fresh solution of sodium hydroxide and leached under above-mentioned conditions.

[0085] The water-washed residue was dried at 90° C. to remove free water.

[0086] b. Results and Discussion

[0087] The results are presented in Tables 1, 2, 3, 4 and 5

TABLE 1

Metal extraction efficiency after leaching the spent catalyst composition oxidised at 700° C. with sodium hydroxide			
Number of the leaching steps	% Cobalt extracted	% Platinum extracted	% Aluminium extracted
1	0.18	0	76.0
2	0.25	0	89.1

Conditions:

Leaching temperature: 170° C.

Leaching time: 4 hr

Leaching pressure: 9 bar

Concentration of sodium hydroxide: 25%

[0088]

TABLE 2

Metal extraction efficiency after leaching the spent catalyst composition oxidised in the presence of sodium carbonate & sodium chloride with sodium hydroxide			
Number of the leaching steps	% Cobalt extracted	% Platinum extracted	% Aluminium extracted
1	0.01	0	70.6
2	0.02	0	85.8

Conditions:

Leaching temperature: 170° C.

Leaching time: 4 hr

Leaching pressure: 9 bar

Concentration of sodium hydroxide: 25%

[0089]

TABLE 3

Metal extraction efficiency after leaching the spent catalyst composition oxidised in the presence of sodium carbonate with sodium hydroxide			
Number of the leaching steps	% Cobalt extracted	% Platinum extracted	% Aluminium extracted
1	0.01	0	71.3
2	0.02	0	86.5

Conditions:

Leaching temperature: 170° C.

Leaching time: 4 hr

Leaching pressure: 9 bar

Concentration of sodium hydroxide: 25%

[0090]

TABLE 4

Metal extraction efficiency after leaching the oxidised spent catalyst composition with a solution of sodium hydroxide			
Number of the leaching steps	% Cobalt extracted	% Platinum extracted	% Aluminium extracted
1	1.4	0	90.1
2	3.0	0	96.6

Conditions:

Leaching temperature: 170° C.

Leaching time: 4 hr

Leaching pressure: 9 bar

Concentration of sodium hydroxide: 50%

[0091]

TABLE 5

Metal extraction efficiency after leaching the oxidised spent catalyst composition in presence of either sodium carbonate or sodium chloride with water			
Number of the leaching steps	% Cobalt extracted	% Platinum extracted	% Aluminium extracted
1	1.7	0	50.6

Conditions:

Leaching temperature: 100° C.

Leaching time: 4 hr

Leaching pressure: atmospheric pressure

[0092] From Tables 1, 2, 3 and 4 it follows that around 70 to 75% of the Al originally present in the spent catalyst were extracted from the oxidised spent catalyst (oxidised with or without the addition of sodium carbonate or sodium chloride) when using a solution of sodium hydroxide (25% w/w NaOH) after one leaching step.

[0093] From Table 1 it can be seen that approximately 89% of the Al present in the spent catalyst were selectively dissolved in a solution of sodium hydroxide (about 25% NaOH) when using high pressure (about 9 bars) and temperature (170 deg) in two leaching steps. Very little cobalt was reported in the leach liquor obtained after the leaching step. No evidence of the platinum was reported in the leach liquor. From Table 4 it follows that 90 to 97% of the Al and 1 to 3% of the Co present in the spent catalyst were selectively dissolved in a solution of sodium hydroxide (about 50% w/w NaOH) after two leaching steps. While almost all Pt are still contained in the washed base-residue.

[0094] It can be seen from Table 5 that about 50.58% of the Al and 1.7% of Co were extracted from the oxidised spent catalyst composition obtained after oxidising the waxy lumps of spent catalyst composition in the presence of sodium carbonate or sodium chloride when using water as a lixiviant. No Pt was reported in the leach liquor obtained after using water as a lixiviant

[0095] It can be concluded that almost of all the Al present in the oxidised spent catalyst composition was selectively extracted from the spent catalyst when using a solution of sodium hydroxide of about 50% w/w NaOH in two leaching steps, whereas almost all of Co and Pt are still contained in the base residue.

3. Flocculation Test on the Slurry From the Caustic Leaching Step.

[0096] After leaching the calcined spent cobalt-based catalyst with a solution of sodium hydroxide (about 25% w/w NaOH) at high temperature (200° C.) and pressure (15 bar), the resulting slurry was formed. This slurry typically contains ultra fine solid particles and sodium aluminate-containing solution. It was filtered with difficulty and might possibly make the proposed process of recovering high value metals not to be technically feasible.

[0097] To resolve this filtration problem import flocculants (HX200; HX300 and HX400) as presently produced by Cytec Industries, Cyanamid were used to flocculate the suspended solids from the slurry. These flocculating reagents (modified anionic polyacrylamides) worked well at high pH (about 12) and improved the sedimentation rate and filterability of the suspended ultra fine solid particles from the slurry.

[0098] a. Experimental Procedure

[0099] The procedure described below was used in all experiments conducted on the slurry to flocculate the suspended ultra fines.

[0100] Approximately 2% w/w of Cytec flocculant was prepared using a solution of sodium hydroxide (about 2% w/w NaOH). The solution was then conditioned at ambient temperature for one hour to form homogeneous solution. It was further diluted with a solution of sodium hydroxide (2% w/w NaOH) to produce a final solution containing about 0.25% w/w of the flocculant.

[0101] Approximately 3000 to 6000 g/t of the modified polyacrylamide (0,25%) heated to 90 degrees Celsius was added to the boiling slurry and mixed thoroughly until the flocs were formed. These flocs were separated from the mixture by filtration and eventually washed with water to remove aluminium-containing filtrate absorbed during the filtration. The turbidity of the filtrate was measured prior to aluminium analysis. The filtrate as well as the dried flocs produced in this way was submitted for aluminium analysis.

[0102] b. Results and Discussion

[0103] The results obtained are given in Table 6 below.

TABLE 6

Turbidity value obtained after the flocculation		
Flocculants	Concentration of flocculants used (g/t)	Turbidity (NTU)
HX200	3000	172.5
HX200	6000	88.4
HX300	3000	146.0
HX300	6000	57.6
HX400	3000	147.0
HX400	6000	109.0

[0104] Visual observation indicated clearly that during the flocculation of the fine solid particles were agglomerated to form the flocs that were filtered rapidly, and resulting in more efficient separation when using Cytec flocculants. It was also visually observed that the flocs formed by Cytec flocculants are fragile and ruptured easily if mixing is too vigorous.

[0105] An adequate mixing is required in order to produce flocs of high mechanical strength that can last throughout the flocculation period.

[0106] ICP analysis conducted on the flocs and the dried filter cake from the original slurry showed clearly that concentrations of aluminium ions in the flocs and dried filter cake were 20% and 21.6% respectively. This implies that no precipitation of the dissolved aluminium species from the solution was experienced during the flocculation step.

[0107] The turbidity value of the original slurry prior to the flocculation was measured to 3000 NTU.

[0108] It is apparent when observing Table 6 that the turbidity value of the filtrate decreases with an increase in the concentration of flocculants during the flocculation step. This significant decrease of the turbidity value indicated clearly that the import flocculants successfully achieved efficient separation of the ultra fine solids from the sodium aluminate-containing solution.

4 Crystallisation of Aluminium Trihydrate (ATH) from Sodium Aluminate.

[0109] a Experimental Procedure

[0110] After leaching the calcined spent catalyst with a solution of sodium hydroxide (about 25% w/w NaOH), the leach liquor containing mainly sodium aluminate was produced. This solution was stored in a one-liter container for a period of one month. Visual observation indicated that

white crystals were formed after keeping the solution for a month. After filtering, washing and drying of the crystals, the final solid sample was submitted for XRD analysis and sent for elemental analysis. Eventually, the filtrate containing mainly sodium hydroxide and small amounts of sodium aluminate can be recycled to the leaching step where it utilizes as a lixiviant.

[0111] b Results and Discussion

[0112] The XRD analysis indicated that Gibbsite $[\text{Al}(\text{OH})_3]$ is present in the crystals. The results also indicated that approximately 99% of the Al present in the sodium aluminate solution was crystallised in the form of Gibbsite. The elemental analysis indicated that aluminium trihydrate with a chemical purity of 99% was produced after crystallisation step. This product complies favourably with the specification of aluminium trihydrate, which is currently produced by Kynochem™ (see Table 7). Aluminium trihydrate is commercially used as a raw material for the production of aluminium chemicals including aluminium sulphate, aluminium chloride, sodium aluminate and alumina. It can also be used as a catalyst.

[0113] In order to further improve the rate of aluminium trihydrate crystallisation, a saturated solution of sodium aluminate should be seeded with a commercial aluminium trihydrate.

5 Calcination of Aluminium Trihydrate to form Alumina.

[0114] a Experimental Procedure

[0115] Aluminium trihydrate produced during the crystallisation step was calined at various temperatures (ranging from 400 to 600 Degrees Celsius) in the presence of air. Following the calcination a white powdered product was formed. Subsequently, both product and alumina were submitted for XRD analysis.

[0116] b Results and Discussion

[0117] The XRD analysis indicated clearly that Boemite was formed at 400 Degrees Celsius whilst Gamma was formed at 600 Degrees Celsius during calcination of the aluminium trihydrate.

TABLE 7

Comparison of calcined aluminium trihydrate with a commercial aluminium trihydrate (ATH)		
Substance	Mass Percentage w/w	
	Commercial ATH	Calcined ATH
Fe_2O_3	<0.2	0.0
MnO	<5 ppm	0.0
Cr_2O_3	—	0.0
V_2O_5	—	0.0
TiO_2	—	0.0
CaO	—	0.11
K_2O	—	0.0
P_2O_5	—	0.0
SiO_2	—	0.0
Al_2O_3	65	64.2
MgO	<1%	0.0
Na_2O	<1%	0.7
Cl	<1%	0.0
S	—	0.0

TABLE 7-continued

Comparison of calcined aluminium trihydrate with a commercial aluminium trihydrate (ATH)		
Substance	Mass Percentage w/w	
	Commercial ATH	Calcined ATH
As	5 ppm	3 ppm
Cu	5 ppm	0.0
Pb	5 ppm	6 ppm
Se	5 ppm	0.0
Cd	<1 ppm	0.0
Zn	<0.1%	19 ppm
F	<0.1%	65 ppm
Hg	<1 ppm	<10 ppb
NO ₃	<0.1%	N.D*
NO ₂	<0.1%	N.D*
CN	<5 ppm	N.D*
Mass Change	-35%	-34.9%

*not determined

6. Selective Dissolution of Cobalt from the Twice-Leached Residue by Nitric Acid—Dissolution of Cobalt Step

[0118] The water washed leached residue recovered from the base leaching step typically contains 51% w/w cobalt, 0.124% w/w platinum and 4.9% w/w aluminium.

[0119] The leached residue is contacted with a solution of nitric acid of about 55% w/v HNO₃ in order to selectively dissolve cobalt.

[0120] ps a. Experimental Procedure

[0121] Approximately 128 g of the water washed leached residue was dissolved into a solution of nitric acid comprising of about 400 g of 55% w/v of nitric acid at 100° Celsius for 4 hr. The experiment was conducted at atmospheric pressure.

[0122] The slurry formed from this leaching step was filtered at room temperature to obtain a filtercake. A washing step was included in the experiment using a filtercake to water ratio of 1:4 to remove the residual leach liquor retained after the leaching step.

[0123] The wash solution was then combined with the leach liquor to form the final parent solution. After drying the washed filtercake, the leached residue was weighed out prior to the cobalt, platinum and aluminium analysis.

[0124] To further improve metal extraction efficiencies, a second leaching step was conducted on the leached residue. In the second leaching step, the leached residue was contacted with fresh nitric acid solution and the leaching of the mixture was then carried out under above-mentioned leaching conditions

[0125] b. Results and Discussion

[0126] The results are given in Table 8. The inductively coupled plasma (ICP) analysis clearly indicated that approximately 84% w/w of the cobalt, 66% w/w of the aluminium and 20% w/w of the platinum present in the water washed leached residue from the base leaching step were successfully dissolved in a solution of nitric acid using a solid to liquid ratio of 1:4 in one leaching step.

TABLE 8

The amount of the cobalt, platinum and aluminium present in the residue before and after leaching step				
Substance	Mass of Substance before leaching step	Mass of substance after the leaching step	Percentage Metals	Percentage Metals
			Extracted after one leaching step	Extracted after two leaching steps
Cobalt	65.28	10.44	84	99.97
Aluminium	6.27	2.11	66	99.7
Platinum	0.16	0.13	20	37.5

[0127] From the leaching results it can be concluded that almost all of the cobalt present in the leached residue were dissolved in a solution of nitric acid. The results also indicated that most of the platinum remained in the leached residue after two leaching steps.

7. Flocculation After the Nitric Acid Leaching Step

[0128] a. Experimental Procedure

[0129] Approximately 2000 g of the acidic leach liquor solution from the leaching step was mixed with 500 ml of 0.1% ZN92V Zetafloc produced by Zetachem Company. The slurry was heated to 60° C. whilst stirring and subsequently conditioned for 10 min. The leach liquor solution was separated from the flocs by decantation method. In order to remove the residual leach liquor solution from the flocs, they were washed with 500 ml of water at 60° C. Finally the flocs were dried at 90° C. and reserved for another treatment. The leach liquor solutions together with the dried flocs were submitted for ICP analysis.

[0130] b Results

[0131] Visual observation clearly indicated that the fine solid particles were agglomerated to form the sticky flocs during the flocculation practice. Following the flocculation of the slurry with ZN92V Zetafloc produced by Zetachem Company the flocs were readily settled down and filtered with ease. Subsequently the decantation method that was utilised during the flocculation step resulted in a good separation of solids and liquid.

8 Crystallisation of the Cobalt Nitrate from the Leach Liquor from the Selective Dissolution of Cobalt from the Base Leached Residue—Crystallisation Step

[0132] The leach liquor from the selective dissolution of cobalt from the base leached residue as well as the purified leach liquor was crystallised to form a red-brown crystalline cobalt nitrate salt Co (NO₃)₂·6H₂O. The filtrate containing free water and nitric acid would be utilised in the crystallisation step of cobalt nitrate or selective dissolution step of cobalt from the water washed—leached residue

[0133] a. Experimental Procedure

[0134] Approximately 150 ml of either impure acid leach liquor or the purified leach liquor was transferred into a 500-ml beaker. This impure acid leach liquor typically contained 68.3 g/l Co, 5.2 g/l Al, 65 mg/l Pt while the purified acid leach liquor contained 326 mg/l Fe, and 7.7 g/l

Co, 18 mg/l Al, 3 mg/l Pt and 4 mg/l Fe. The leach liquor was heated to 90° C. until its volume was reduced by 50%. The concentrated leach liquor was then added to a 250-ml crystalliser and on cooling off the solution, red-brown crystals were formed.

[0135] The crystals were separated by normal filtration and dried at 55° C. to further improve their crystallinity. Subsequently, the dried crystals were submitted to XRD analysis and elemental analysis. Concentrations of the substances present in the crystals were reported as percentage (% w/w) in Table 9.

[0136] b. Results and Discussion

[0137] Visual observation clearly indicated that red-brown crystals were formed after cooling off the concentrated leach liquor at room temperature.

[0138] The XRD analysis showed clearly that cobalt nitrate hydrate, $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is present in the cobalt nitrate samples. The results are presented in Table 9 below.

[0139] It is apparent from the results in Table 9 that the pure cobalt nitrate produced after using the solvent extraction compare more favourably to the commercially available cobalt nitrate in terms of the chemical purity. However the pure and impure cobalt nitrate salts contained high level of the calcium oxide. This impurity may possibly attributed to the addition of calcium oxide during the calcination step. The results also clearly indicated that the concentration of cobalt in the impure cobalt nitrate crystals is low. This may possibly be contributed to the low retention time of the crystals during the drying step and also low concentration of nitric acid used during the dissolution step.

TABLE 9

Composition of crystallised and commercially available cobalt nitrate.			
Substances	Commercial Cobalt nitrate Mass Percentage (% w/w)	Impure Cobalt nitrate Mass Percentage (% w/w)	Pure Cobalt nitrate Mass Percentage (% w/w)
Fe_2O_3	0.02	0.3	0.00
MnO	0.02	0.02	0.02
Cr_2O_3	0.02	0.04	0.00
V_2O_5	0.01	0.01	0.00
TiO_2	0.00	0.20	0.00
CaO	0.05	1.00	0.70
K_2O	0.00	0.00	0.00
P_2O_5	0.00	0.00	0.00
SiO_2	0.00	0.00	0.00
Al_2O_3	0.00	2.00	0.00
MgO	0.00	0.00	0.00
Na_2O	0.00	0.20	0.00
Cl	0.00	0.00	0.00
Pt	0.00074	0.00066	0.0003
Co	22.8	16.30	20.00
S	0.10	0.10	0.10

[0140] The crystallisation of cobalt nitrate from the leach liquor produced from the dissolution step was proved successful.

[0141] To increase the concentration of cobalt in the impure cobalt nitrate crystals, the retention time of the crystal at 55° C. may be increased. This may remove free water retained in the crystals after the filtration. Eventually, an excess of nitric acid should be used during the crystallisation step.

9 Precipitation of Fe and Al Ions from the Impure Cobalt Nitrate Containing Solution.

[0142] In order to prevent the loading of Fe and Al into an organic phase during the solvent extraction step, the precipitation of both Fe and Al ions from the impure cobalt containing solution should be firstly conducted. The impure cobalt containing solution from the dissolution of the base leached residue step typically 5.2 g/l Al 0.065 g/l Pt, 0.326 g/l Fe and 68 g/l Co. A solution of ammonium hydroxide (about 25% w/v NH_4OH) would be used to selectively precipitate both Fe and Al ions from the cobalt-containing solution. The filtrate produced in this way could be used in the solvent extraction step where the cobalt ions will be selectively loaded into an organic phase under certain conditions. Subsequently the precipitate containing both Fe and Al formed after the addition of ammonium hydroxide to the impure cobalt-containing solution will be dissolved in a solution of sodium hydroxide to form sodium aluminate. This aluminate can be recycled in the precipitation of aluminium hydroxide step. A dumping option should be considered for sodium hydroxide insoluble precipitate containing mainly iron hydroxide, which is environmentally friendly by-product. The sodium hydroxide insoluble precipitate may be reserved for the platinum dissolution

[0143] a Experimental Procedure

[0144] Approximately 200 g of the impure cobalt-containing solution was transferred to a 1000 cm^3 beaker. A solution of ammonium hydroxide (about 25% m/v NH_4OH) was used to adjust the pH of the impure cobalt-containing solution at 50 degrees Celsius. Upon the addition of ammonium hydroxide to the impure cobalt-containing solution, a gelatinous brown precipitate was formed at different pH values (ranging from 4 to 5). This precipitate was then separated from the solution by normal filtration and subsequently washed with enough water to remove the residual solution retained after filtration. The wash solution and the filtrate were combined at room temperature to form the final filtrate. This filtrate typically contains cobalt nitrate and ammonium nitrate is reserved for the solvent extraction step. The portion of the filtrate was prepared and eventually submitted for cobalt, aluminium and iron analysis.

[0145] The precipitate containing typically Fe and Al was allowed to react with sodium hydroxide (about 25% m/v of NaOH) to form sodium aluminate which is eventually recycled to the precipitation of aluminium hydroxide step. While the sodium hydroxide insoluble precipitate, which contains Fe, may possibly be dumped or dissolved in a solution of sulphuric acid or nitric acid to form iron salts that are suitable for water purification.

[0146] b Results and Discussion

[0147] The results are given in Table 11 where it can be clearly seen that the precipitation efficiency of the metal ions increases with an increase in the pH value of the impure cobalt-containing solution. The results also indicated that almost all of the Fe and Al present in the solution were successfully precipitated at pH 5.0 at 50 Degrees Celsius.

TABLE 11

The precipitation efficiency of metal ions at various pH when using ammonium hydroxide.				
pH value	% Co precipitated	% Pt precipitated	% Al precipitated	% Fe precipitated
4	2.2	38.5	88.3	93.9
4.5	8.1	51.5	98.73	97.4
5	28.4	89.3	98.1	97.0

10 Purification of the Filtrate from the Precipitation Step by Solvent Extraction Method—Cobalt Nitrate Purification Step

[0148] The original aqueous filtrate from the precipitation step typically contains Co, Pt, Al, Fe, NO_3^- and NH_4^+ ions.

[0149] a. Experimental Procedure

[0150] The organic phase salt which is suitable for the extraction of the Co ions was prepared as follows: 1000 ml of ammonium hydroxide solution (about 12.5% w/v NH_4OH) was contacted with an equal volume of the organic phase containing 40% w/w DEHPA, 20% w/w TriButylPhosphate (TBP) and 40% w/w illuminating paraffin at room temperature. This mixture was stirred for 15 min. The two phases were allowed to separate at room temperature. The organic phase salt produced in this way contains ammonium ions and is suitable for the extraction of Co ions from the filtrate at pH 4.

[0151] Approximately 50 ml of the filtrate containing 18 mg/l Al, 4 mg/l Fe, 7.7 g/l Co and 3 mg/l Pt was transferred to a 1000 ml beaker. The pH of the filtrate was initially measured to be 4.1 at 70° C. Approximately 400 ml of the organic phase salt was contacted with 50 ml of the original aqueous filtrate at 70° C. and was subsequently shaken for 5 min. The two phases were allowed to cool to a room temperature and eventually separated. The aqueous phase recovered after solvent extraction experiment was submitted for the determination of Al, Pt, Co and Fe ions using ICP instrument.

[0152] The loaded organic phase produced in this experiment could possibly be utilised in the stripping step where finally cobalt nitrate will be produced.

[0153] b. Results and Discussion

[0154] Visual observation clearly indicated that no emulsion or third phase formation was experienced during the solvent extraction step. Also, the phase separation was acceptable for all tests conducted.

[0155] The colour of the mixture (organic phase and aqueous phase) turned to pink at low temperature (ranging from 30 to 45° C.) during the solvent extraction experiment. However, at high temperature (ranging from 50 to 90° C.) its colour changed from pink to blue. The pink colour indicates the presence of octahedral cobalt complex in the mixture whilst the blue indicates tetrahedral cobalt complex. It is therefore considered that the colour change is definitely attributed to a change in co-ordination state of the cobalt complex.

[0156] After phase separation the colour of the loaded organic phase still remained blue even if the temperature of the loaded organic phase was lowered to an ambient temperature.

[0157] The results are given in Table 12 below. From the results it is apparent that almost all of Co and Al ions present in the original aqueous filtrate were extracted into the organic phase during the solvent extraction. Also, all of the Pt ions present in the original aqueous filtrate were loaded into the organic phase when using the solvent extraction at an original aqueous filtrate to organic phase ratio of 1:8. It is also interesting to note that only 52% of the Fe ions present in the original aqueous filtrate were extracted by the organic phase. This implies that some of the Fe ions present in the original aqueous filtrate are in the oxidation state of +2. The Fe (II) ions that are present in the aqueous filtrate are not easily extracted by organic phase containing di-(2ethylhexyl) phosphoric acid under any conditions during solvent extraction experiment.

TABLE 12

Extraction efficiency of metal ions from the original aqueous filtrate by solvent extraction.	
Substance	% Metal extracted
Al	94.9
Co	99.9
Pt	100.0
Fe	52.0

[0158] It can be concluded that solvent extraction method gave good performance in terms of both Co and Pt ions extraction efficiency and phase separation when using di-(2-ethylhexyl) phosphoric acid as an extractant and tributyl phosphate as a modifier.

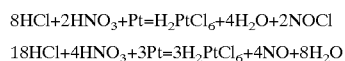
11 Platinum Dissolution

[0159] The literature review clearly cites that the platinum from the Platinum Group Metals (PGM) ore is not acted upon by oxygen under any conditions and it is not attacked by ordinary acids. There are two possible commercial processes for the dissolution of the Pt, namely dissolution of the Pt in aqua regia (solution of HCl and HNO_3) and in HCl and $\text{Cl}_2/\text{H}_2\text{O}_2$.

[0160] Pt can dissolve in 6 to 18 M aqua regia at 80 to 90 Degrees Celsius at atmospheric pressure to form a chloroplatinic acid, H_2PtCl_6 . To avoid the solution of oxidising acids to boil violently and overflow during the experiment, 6 M acid solution is used. The platinum acid obtained in this fashion could be reserved for the preparation of platinum sponge and various salts.

[0161] The platinum dissolution in aqua regia is preferred because the yield of the Pt from the ore is around 99%.

[0162] The following reactions takes place in aqua regia:



[0163] a. Experimental Procedure

[0164] The residue produced during the nitric acid leaching was firstly calcined at 700° C. for 6 h to oxidise the flocculent present in the residue. Subsequently 20 g of the nitric acid insoluble residue containing 7.67% Pt was dissolved in 1000ml of aqua regia ($3\text{HCl} : 1\text{HNO}_3$) at 80° C. to 90° C. at atmospheric pressure for 4 hr to form a chloroplatinic acid, H_2PtCl_6 . The latter was separated from the

aqua regia insoluble residue through filtration. The platinum acid obtained in this fashion could be reserved for the preparation of platinum sponge and various salts. The blue insoluble residue formed during the dissolution of platinum was dried at 90° C. prior to the submission for XRD analysis.

[0165] b. Results

[0166] The results of the residue obtained during the leaching of nitric acid residue with aqua-regia solution are presented in Table 13 below.

TABLE 13

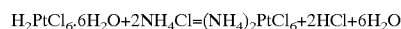
Composition of residue obtained after leaching nitric acid residue with aqua-regia solution.	
Substance	Mass Percentage (m/m)
Fe ₂ O ₃	1.38
MnO	0.06
Cr ₂ O ₃	0.26
V ₂ O ₅	0.01
TiO ₂	0.51
CaO	0.31
K ₂ O	0.02
P ₂ O ₅	0.00
Al ₂ O ₃	36.20
SiO ₂	28.60
MgO	0.20
Na ₂ O	0.10
Cl	3.00
S	0.10
Co	12.40
Pt	<0.01
Mass Change (g)	15.30

[0167] It can be seen from Table 13 that the residue obtained during the aqua regia leaching does contain Pt species. This implies that almost all of the Pt present in the nitric acid insoluble residue was successfully dissolved in the aqua-regia solution. The XRD analysis clearly indicated that cobalt aluminate (spinel) is present in the residue obtained after leaching the nitric acid residue with aqua-regia solution.

12 Precipitation of Platinum from Chloro Platinic Acid, H₂PtCl₆

[0168] A solution of ammonium chloride (about 25%) is used to quantitatively precipitate the Pt(IV) from a platinic acid at 50 to 70 Degrees Celsius in the form of ammonium chloroplatinate, (NH₄)₂PtCl₆ (deep-yellow colour). The deep-yellow crystals are recovered with a purity of 99 to 99.5% in greater than 99% yield.

[0169] The following reactions take place between ammonium chloride and a solution of chloroplatinic acid:



[0170] a. Experimental Procedure

[0171] Initially chloroplatinic acid solution (1000ml) was heated to 90° C. to remove unreacted nitric acid. On cooling off the crystals were formed. Approximately 100 ml of hydrochloric acid was added to the crystals and the mixture was further evaporated to remove the remaining nitric acid from the crystals. A solution of ammonium chloride (about 25%)(a stoichiometric amount) was used to quantitatively

precipitate the Pt (IV) from a platinic acid at 50° C. to 70° C. in the form of ammonium hexachloroplatinate, (NH₄)₂PtCl₆ (deep-yellow colour). The deep-yellow crystals were isolated from the solution through filtration. The crystals were dried at 50° C. and submitted for XRD and XRF analyses respectively. The percentage yield of platinum from the spent catalyst was then calculated and reported as a percentage.

[0172] b. Results

[0173] The XRD analysis showed clearly that diammoniumhexachloroplatinate, (NH₄)₂PtCl₆ is contained in the deep-yellow precipitate formed during the addition of ammonium chloride to the chloroplatinic acid. The XRF results on diammoniumhexachloroplatinate originating from the spent catalyst are presented in Table 14 below.

TABLE 14

Composition of diammoniumhexachloroplatinate produced through the sodium-nitric acid leaching process.	
Substance	Mass Percentage (m/m)
Fe ₂ O ₃	0.44
MnO	0.00
Cr ₂ O ₃	0.04
V ₂ O ₅	0.00
TiO ₂	0.03
CaO	0.09
K ₂ O	0.07
P ₂ O ₅	0.11
Al ₂ O ₃	5.10
SiO ₂	0.5
MgO	0.00
Na ₂ O	0.00
Cl	22.50
S	0.70
Co	0.80
Pt	46.10

[0174] It can be seen from Table 14 that diammoniumhexachloroplatinate precipitated with trace amounts of impurities like Fe, Cr, Ti, Ca, K, P, Si, S and Co. Approximately 5,10% alumina still contained in the latter.

[0175] From the aforementioned results obtained when using the sodium hydroxide-nitric acid leaching, it can be followed that Pt salt was successfully recovered from the spent catalyst. This product could be converted into a tetraamine platinum nitrate, which may possibly be used in the new catalyst preparation for the FT process.

13. Reduction of Pt(IV) to Pt-Metal

[0176] a. Experimental Procedure

[0177] Approximately 0,2 g of diammonium hexachloroplatinate was accurately weighed out on the analytical balance and added into a silica crucible. The sample was heated to 800 degrees Celsius for one hour. Subsequent to the cooling of the heated sample, it was submitted to SCL laboratory for XRD analysis.

[0178] b. Results obtained

[0179] The XRD analysis indicated clearly that metallic platinum is present in the calcined product. This product can in future be used in the production of platinum (II) salts like

platinum nitrate. It is interesting to note that platinum was not oxidised under afore-mentioned conditions to form platinum oxide.

TABLE 15

The extraction efficiency of metal ions during the Sodium hydroxide-nitric acid-aqua regia leaching process.		
Recovery % Al	Recovery % Co	Recovery % Pt
99.75	99.78	91.70

[0180] From Table 15 the overall efficiency of the process can be seen.

1. A process for the selective recovery of aluminium, cobalt and platinum, and compounds thereof, from a catalyst composition including aluminium, cobalt and platinum, said process including the steps of:

treating the catalyst composition to selectively get ions of substantially only one of the aluminium, cobalt and platinum into solution;

recovering, in separate process steps, the thus treated aluminium, cobalt, or platinum in salt or metal form; and

repeating the treating and recovering steps for each of the aluminium, cobalt and platinum.

2. A process for the selective recovery of aluminium, cobalt and platinum, and compounds thereof, from a catalyst composition including aluminium, cobalt and platinum, said process including the steps of:

oxidising substantially all organic material present with the catalyst composition;

leaching the aluminium and/or compounds thereof from the oxidised catalyst composition with a strong or weak base to form an aluminium containing product and a filtrate;

filtering of alkali insoluble residue from the filtrate;

washing of the alkali insoluble residue with water to remove the residual alkali aluminate solution;

precipitating of silica from alkali aluminate with slaked lime or quicklime;

filtering of insoluble silicate from alkali aluminate;

crystallising aluminium trihydrate from the alkali aluminate solution;

filtering aluminium trihydrate crystals from the alkali aluminate solution

recycling of the alkali solution to the leaching step;

dissolving the cobalt and compounds thereof present in the water washed-insoluble residue composition with an inorganic acid;

separating a substantial portion of the cobalt rich solution from a solid component present after the dissolving step;

precipitating substantially all non-cobalt and/or non-cobalt compound impurities from the cobalt rich solution;

crystallizing the cobalt and/or cobalt compounds out of the cobalt rich solution to form impure cobalt nitrate salt; or

as an alternative to the crystallizing step, selectively loading substantially all cobalt ions from the impure cobalt rich solution into an organic phase by solvent extraction;

subsequently stripping the cobalt-containing organic phase with a solution of nitric acid to form a pure cobalt nitrate salt;

dissolving the platinum and compounds thereof and non-cobalt and/or non-cobalt compound impurities from the cobalt rich solution out of the water washed solid component to obtain a platinum rich solution; and

recovering platinum and/or platinum salts from the platinum rich solution.

3. A process as claimed in claim 2, wherein after the aluminium leaching step and prior the alkali insoluble residue filtration step, a flocculation step is included to remove ultra fine solids which inhibit efficient filtration.

4. A process as claimed in claim 2 or claim 3, wherein after the cobalt dissolution step and prior to the separation of a substantial portion of the cobalt rich solution, a flocculation step is included to remove ultra fine solids which may inhibit efficient separation.

5. A process as claimed in claim 3, wherein the flocculation is carried out with the aid of flocculating agents selected from a group including modified anionic polyacrylamides.

6. A process as claimed in claim 3 or claim 5, wherein the flocculation is carried out at a pH of about 12.

7. A process as claimed in any one of claims 2 to 6, wherein for the oxidising step, the catalyst composition is heated to a temperature of between 600° C. and 1400° C., generally between 700° C. and 1000° C.

8. A process as claimed in any one of claims 2 to 7, wherein where the catalyst composition is Co/Pt/Al₂O₃/SiO₂, then the oxidised spent catalyst composition contains about 0.0125 g Pt per 100 g Al₂O₃ to 0.175 g Pt per 100 g Al₂O₃ and from 5 g Co per 100 g Al₂O₃ to 70 g Co per 100 g Al₂O₃.

9. A process as claimed in any one of claims 2 to 8, wherein the leaching of the aluminium and/or the aluminium compounds from the oxidised spent catalyst composition is carried out with a solution of sodium hydroxide of about 20% to 50% w/w NaOH, generally 25%, at a temperature ranging from 110° C. to 250° C., typically 200° C., and at a high pressure ranging from 5 to 20 bar, typically 15 bar, with substantially no dissolution of cobalt and platinum from the spent catalyst composition.

10. A process as claimed in claim 9, wherein the leachate is in the form of a slurry.

11. A process as claimed in any one of claims 4 to 10, wherein the flocculation of the slurry prior to filtration is carried out using a flocculant solution prepared from approximately 2% w/w of flocculant which in turn is prepared using a solution of sodium hydroxide of about 2% w/w NaOH, whereafter the flocculant solution is conditioned at ambient temperature for one hour to form homogeneous solution, whereafter it is diluted with a solution of sodium hydroxide of 2% w/w NaOH to produce a final solution containing about 0.25% w/w of the flocculent.

12. A process as claimed in any one of the preceding claims, wherein water leaching is used to selectively solubilize sodium aluminate formed during the oxidising of the spent catalyst in the presence of either sodium carbonate or sodium chloride.

13. A process as claimed in claim 12, wherein the water leaching is carried out at 50° C. at atmospheric pressure.

14. A process as claimed in claim 12 or claim 13, wherein a solution of sodium aluminate from the water leaching step is reserved for the precipitation of aluminium hydroxide.

15. A process as claimed in any one of claims 12 to 14, wherein the water-washed base insoluble residue is used in the strong or weak inorganic acid cobalt dissolving step.

16. A process as claimed in any one claims 2 to 15, wherein the leached residue recovered from the aluminium leaching step contains 51% w/w cobalt, 0.124% w/w platinum and 4.9% w/w aluminium.

17. A process as claimed in any one of the preceding claims, wherein cobalt recovery is initiated by dissolving the cobalt and compounds thereof present in the water-washed leached residue of the oxidised catalyst composition with a strong acid.

18. A process as claimed in claim 17, wherein the water washed-leached residue is contacted with a solution of nitric acid of about 55% w/v HNO₃ at a temperature of between 80° C. and 200° C. and at a pressure of between 1 bar and 20 bar, in order to selectively dissolve cobalt.

19. A process as claimed in claim 18, wherein the cobalt dissolution step is carried out at 100° and 1 atmospheric pressure.

20. A process as claimed in claim 17, wherein including the separating of a substantial portion of the impure cobalt nitrate as the cobalt rich solution, from the strong acid insoluble residue in the form of the solid component present after the dissolving step.

21. A process as claimed in claim 20, wherein the separation includes a precipitation step during which impurities are precipitated out of the cobalt rich solution.

22. A process as claimed in claim 20 or claim 21, wherein the separation is aided by flocculating using a suitable flocculant used as 0.1% w/w solution.

23. A process as claimed in any one of claims 17 to 22, wherein the cobalt rich solution is purified by selectively removing substantially only cobalt ions from the cobalt rich

solution by solvent extraction so that the cobalt rich solution from the precipitation step typically contains Co, Pt, Al, Fe, N₃⁻ and NH₄⁺ ions.

24. A process as claimed in claim 23, wherein a suitable type of an acidic extractant is used.

25. A process as claimed in claim 24, wherein the acidic extractant is di-(2-ethylhexyl) phosphoric acid (DEHPA) and tributylphosphate (TBP) as a modifier in illuminating paraffin for extracting Co ions from the cobalt rich solution.

26. A process as claimed in claim 24 or claim 25, wherein the solvent extractant is used as an ammonium salt which assists in keeping the pH of the mixture relatively constant after contacting the acidic cobalt rich solution with the organic extractant phase.

27. A process as claimed in any one of claims 23 to 26, wherein the aqueous phase recovered from the solvent extraction is used in the precipitation of Fe and Al ions step, while the loaded organic phase containing mainly Co ions is reserved for a stripping step.

28. A process as claimed in claim 27, wherein the Co loaded organic phase is contacted with a solution of the stripping agent to remove the extracted species.

29. A process as claimed in any one claims 2 to 28, wherein the purified cobalt rich solution is crystallised to form a red-brown crystalline cobalt nitrate salt, Co(NO₃)₂·6H₂O or Co(NO₃)₂·4H₂O depending on the retention time when heating the crystals at 55° C.

30. A process as claimed in any one of claims 2 to 29, wherein platinum is recovered from the nitric acid insoluble solid component from the cobalt dissolution step by dissolving the platinum and compounds thereof and non-cobalt and/or non-cobalt compound impurities from the cobalt rich solution out of the solid component to obtain a platinum rich solution.

31. A process as claimed in claim 30, wherein the dissolved platinum is precipitated out of the platinum rich solution by to form platinum salts complex which can be recovered by a liquid: solid separation process.

32. A process substantially as hereinbefore described and illustrated.

33. A new process substantially as hereinbefore described.

* * * * *