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The selective dissolution and recovery of high value metals from Sasol proprietary spent cobalt catalyst and subsequent characterisation of the products formed

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contained mostly cobalt(II) species. Liptrot (1983) and Donaldson (2001) elucidated that the cobalt(II) hydroxides can be readily precipitated as a blue solid by adding sodium hydroxide solution to a cobalt containing solution. ICP analysis shows that the platinum species did not dissolve in sodium hydroxide solution under the above-mentioned experimental conditions.

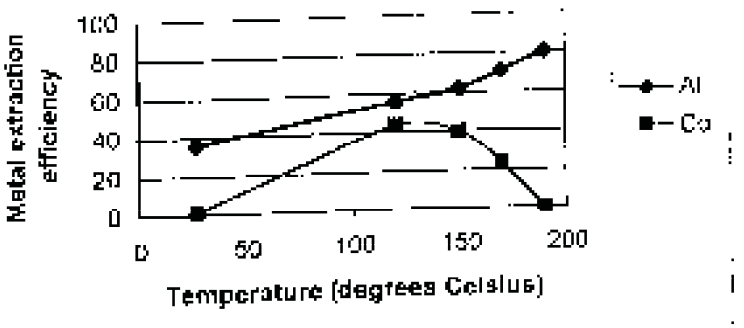


Figure 3.4: Temperature vs. metal extraction efficiency

3.2.1.2 Effect of leaching time on metal solubilisation

It is apparent from Figure 3.5 that aluminium extraction efficiency increased slightly with an increase in the leaching time. The increase in the percentage of aluminium species extracted after one hour is however relatively small, especially if one takes into account the amount of energy that is needed to maintain the temperature at 190 °C for several hours. In contrast, the cobalt extraction efficiency decreased with an increase in the leaching time but eventually increased slightly after three hours of leaching.

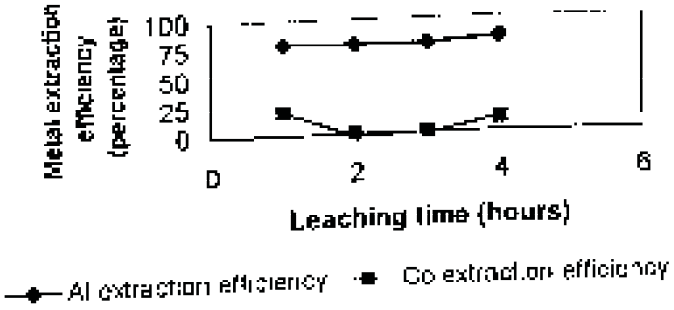


Figure 3.5: Leaching time vs. metal extraction efficiency

It can be concluded that the selective dissolution of aluminium species with sodium hydroxide solution (about 25 % NaOH) at elevated temperature (approximately 190 °C) and pressure (12 bar) from the spent cobalt-containing catalyst could be effected. From Figures 3.4 and 3.5 it follows that the leaching temperature and duration can have significant effects on aluminium species solubilisation and a detrimental effect on cobalt species solubilisation

3.2.2 Leaching of the calcined spent catalyst with hydrochloric acid solution

A solution of hydrochloric acid (about 15 % HCl) was used to selectively dissolve cobalt with substantially no dissolution of alumina from the calcined spent catalyst. The main advantage of this option is that a pure cobalt chloride would be formed and this could be roasted at elevated temperatures to produce a pure cobalt oxide and hydrochloric acid vapours. The cobalt oxide could be dissolved in nitric acid solution to form cobalt nitrate solution. It is envisaged that this solution could subsequently be used in the new catalyst preparation step. The hydrochloric acid vapours will be absorbed into water for subsequent cobalt dissolution.

The ICP analysis indicated clearly that approximately 17 % of Al and 13 % of Co present in the calcined spent cobalt catalyst were simultaneously dissolved in hydrochloric acid solution when using a solid to liquid ratio of 1:1. A solid to liquid ratio of 1:4 gave Al and Co recoveries of around 30 and 31 % respectively. During two leaching steps approximately 48 - 61 % of Al and 56 - 60 % of Co present in the calcined spent cobalt catalyst were successfully solubilised in hydrochloric acid solution using a solid to liquid ratio of 1:4. Freeman (1988), Carson et al (1979), Burkin (1987) and Burnet et al (1984) stated that aluminium and cobalt species dissolves simultaneously in mineral acid solution such as hydrochloric acid.

3.2.3 Leaching of the calcined spent catalyst with nitric acid solution

A solution of nitric acid of about 20 % w/w HNO_3 could be used to selectively dissolve aluminium oxide at 90 °C at atmospheric pressure with substantially no dissolution of cobalt and platinum from the calcined spent catalyst. After the leaching step, the leach liquor solution containing mainly aluminium nitrate was reserved for the precipitation step of aluminium hydroxide. The nitric acid insoluble residue, which will typically contain cobalt and platinum, would be reserved for the selective dissolution step of the metals. The experimental procedure described earlier in Paragraph 2.2.4 was used to selectively dissolve aluminium species from the calcined spent catalyst

From Figure 3.6 it follows that about 52 % of Al and 40 % of Co present in the calcined spent catalyst were simultaneously dissolved in nitric acid solution at 90 °C at atmospheric pressure. These preliminary results supported the literature results of Freeman (1988), Canon et al (1979), Burkin (1987) and Burnet et al (1984). It was stated that aluminium and cobalt species dissolve simultaneously in mineral acid solution.

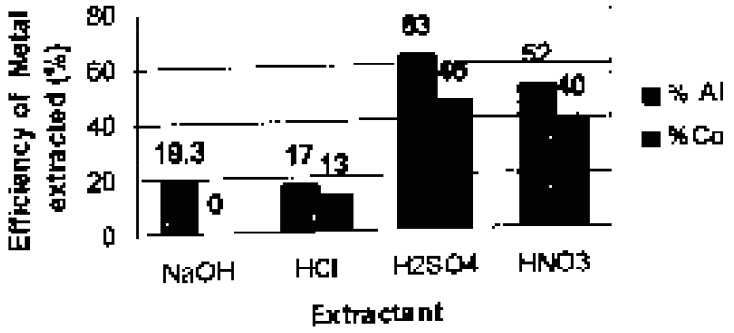


Figure 3.6: Extraction efficiencies of the Al and Co species obtained at 90 °C during the leaching of the spent catalyst with various laiviants.

3.2.4 Leaching of the calcined spent catalyst with sulphuric solution

The experimental procedure described earlier in Paragraph 2.2.5 was used to selectively dissolve aluminium species from the calcined spent catalyst. It is apparent from Figure 3.6 that about 63 % of Al and 46 % of Co present in the calcined spent catalyst were dissolved in a solution of sulphuric acid during one leaching step. These preliminary results show that both aluminium and cobalt species dissolves rapidly in sulphuric acid solution to form metal salts in comparison with nitric acid and hydrochoric acid. To selectively separate the Al and Co species from the sulphate solution, a selective precipitation method should be used. The addition of a strong base such as sodium hydroxide or an ammonium hydroxide during the precipitation step will definitely result in the production of large amounts of salts as by-products. The market for these salts is currently declining and so this option is not attractive.

It is therefore recommended that no further test work should be conducted on the calcined spent catalyst when using sulphuric acid as a lixiviant during the leaching step.

3.2.5 Leaching of the calcined spent catalyst with water

Water leaching could be used to selectively dissolve sodium aluminate or sodium silicate formed during the calcination of the spent catalyst in the presence of either sodium carbonate or sodium chloride. In this approach a solution of sodium aluminate solution would be reserved for the precipitation step of aluminium hydroxide while the residue would be in the nitric acid leaching step.

The experimental procedure described earlier in Section 2.2.6 was followed in order to selectively dissolve aluminium species from the calcined spent catalyst. The results indicate clearly that about 50,6 % of the aluminium species and 1,7 % of the cobalt species were extracted from the calcined spent catalyst obtained after calcining the waxy lumps of spent catalyst with sodium carbonate when using

water as a lixiviant (see Table 3.6). No platinum species were detected in the leach liquor solution obtained after using water as a lixiviant.

3.2.6 Flocculation of the slurry from the alkaline and acid leaching steps

The flocculation results obtained on three different slurries produced during the leaching of the spent catalyst and leached spent catalyst (residue from sodium hydroxide leaching step) are presented and discussed as follows:

3.2.6.1 Flocculation of the sodium aluminate slurry from the alkaline leaching step

In order to resolve the filtration problem, different types of the flocculants that are currently manufactured or sold locally to different water treatment companies were evaluated to flocculate the ultra-fine solids from the aluminium containing slurry. The aluminium species present in the slurry are expected to remain in the solution during the flocculation step. Visual observation indicated that no flocs (agglomerated solids) were formed during the application of the local flocculants. This may be attributed to a significantly high pH value (about 12) of the slurry. Flocculants that are being produced locally only work properly in media having a pH value of around 7 (Adams et al. 1986).

To further resolve the filtration problem, imported flocculants (i.e. HX200; HX300 and HX400), presently produced by Cytec Industries, were used to flocculate the suspended solids from the slurry. These flocculating reagents (modified anionic polyacrylamides) work quite well at high pH (about 12) and it was believed that they would further improve the sedimentation rate and filterability of the suspended ultra-fine solid particles from the slurry (Adams et al, 1986).

The experimental procedure described earlier in Paragraph 2.2.7 was followed to flocculate the suspended solid particles from the sodium aluminate slurry.

The results obtained are presented in Table 3.7 below.

Table 3.7: Turbidity value obtained after the flocculation

Flocculants	Concentration of flocculants used (g/t)	Turbidity of the sample (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

Visual observations indicated that fine solid particles were agglomerated to form the flocs that could readily be filtered, and eventually resulting in more efficient separation when using Cytec flocculants. It was also seen that the flocs formed by Cytec flocculants are fragile and ruptured easily if the mixing is too vigorous. An adequate mixing is required in order to produce flocs of high mechanical strength that can survive throughout the flocculation period.

ICP analysis conducted on the flocs and the dried filter cake from the original slurry showed 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 occurred during the flocculation step. Despite reports by Adams, et al (1986) that typical dosages of anionic flocculants are 1 - 500 g/t. Dosages in the range of 3000 - 6000 g/t of Cytec flocculants were used to flocculate ultra-fines from the slurry formed after using sodium hydroxide to leach alumina from the spent catalyst. The need for application of high dosage of anionic flocculants during flocculation testwork can possibly be attributed to the high percentage

solids (15 %) present in the original slurry. This was confirmed by the high turbidity value (3000 NTU) of the original slurry measured prior to the flocculation. It is apparent from Table 3.7 that the turbidity value of the filtrate decreases with an increase in the concentration of flocculants during the flocculation step. This significant decrease in the turbidity value of the filtrate indicated that the imported flocculants successfully achieved efficient separation of the ultra-fine solids obtained from the sodium aluminate-containing solution.

In conclusion, all the modified flocculants that are currently produced by Cytec can be efficiently used to flocculate ultra-fines suspended in the slurry at a pH value ranging from 11 - 12. The efficient separation of the ultra-fine solids from the slurry was achieved during the flocculation step. It is imperative to optimise the dosages of the evaluated Cytec flocculants during piloting of the proposed process in order to bring an additional reduction in flocculants costs. This may significantly improve process performance.

3.2.6.2 Flocculation of cobalt nitrate slurry from the nitric acid leaching step

The experimental procedure described earlier in Paragraph 2.2.7 was followed in order to flocculate the suspended solid particles from the cobalt nitrate slurry. Visual observation indicated that heavy flocs were readily formed during the flocculation of the suspended ultra-fine solids with ZN92V Zetafloc produced by Zetachem. The flocs produced in this manner settled down rapidly and eventually the decantation method was applied to separate the flocs from cobalt nitrate solution. It was observed that the flocs are sticky and that they survived throughout the flocculation period.

3.2.7 Selective dissolution of the cobalt from the basic leached residue by nitric acid solution

The 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.

Owing to the fact that cobalt is environmentally toxic and the high cost of platinum, dumping is not a viable option (Seiler and Sigel 1988). Further, both cobalt and platinum are high value metals. Renner (2001) stated that cobalt oxide could react with a solution of nitric acid to form cobalt nitrate, which is a red-brown crystalline compound. In an attempt to selectively dissolve cobalt, the leached residue was contacted with a solution of nitric acid (about 55 % w/v HNO_3). The impure cobalt nitrate solution produced in this manner can be used in the new catalyst preparation step after purification. This product may also be used in the chemical or ceramics industries and for the production of high purity cobalt for use in the electronics and related industries. The nitric acid insoluble residue, which is mainly composed of platinum, could be used to prepare platinum compounds. Renner (2001), McDonald and Hunt (1982), Hartley (1973), Seiler and Sigel (1988) and Edwards (1976) pointed out that platinum dissolves completely in an aqua-regia (HNO_3-HCl) medium but is not soluble in single mineral acid..

The experimental procedure described earlier in Section 2.2.8 was used in order to selectively dissolve cobalt species from basic leached residue. The results are presented in Table 3.8. The ICP analysis 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 leached residue (containing 51 % w/w cobalt, 0,124 % w/w platinum and 4.9 % w/w aluminium) from the base leaching step were successfully dissolved in nitric acid solution using a solid to liquid ratio of 1:4 in one leaching step. Although Renner (2001), McDonald and Hunt (1982), Hartley (1973), Seiler and Sigel (1988) and Edwards (1976) reported that the crystalline platinum does not dissolve in nitric acid solution, it was observed in the present studies that trace amounts of platinum (about 20 % w/w) were soluble in nitric acid solution.

Table 3.8: The amounts of cobalt, platinum and aluminium present in the calcined spent catalyst and residue before and after the leaching step.

Element	Mass of element in calcined spent catalyst (g)	Mass of element in residue after one leaching step (g)	Mass of element in residue after two leaching steps (g)
cobalt	65.3	10.4	0.02
aluminium	6.27	2.14	0.02
platinum	0.16	0.13	0.10

From the leaching results contained in Table 3.8, it can also be seen that almost all of the cobalt and aluminium species present in the leached residue were successfully dissolved in nitric acid solution during the two leaching step. These results also indicated that most of the platinum species still remained in the twice-leached residue.

3.2.8 Platinum dissolution

The procedure described earlier in Section 2.2.9 was followed in order to selectively dissolve platinum species from the nitric acid residue. The results on the residue obtained during the leaching of nitric acid residue with an aqua-regia solution are presented in Table 3.9 below. From visual observation, the slurry formed during the leaching step was filtered with ease. The filtrate produced in the experiment contains platinic acid. It can be seen from Table 3.9 that the residue obtained during the aqua regia leaching contains trace amount of platinum species. This implies that almost all platinum species present in the nitric acid insoluble residue were successfully dissolved in the aqua regia

solution. Table 3.9 also shows that low levels of many impurities such as Mn, Fe, Cr, V, Ti, Ca, K, Mg, Na and S species are to be found in the aqua-regia insoluble residue. From Table 3.9, it follows that the residue contains 36,2 % Al_2O_3, 28,6 % SiO_2, 3% Cl and 12,4 % Co. The chloride ions present in the aqua-regia insoluble residue are definitely originating from the aqua regia, which contains both nitric acid and hydrochloric acid. The XRD analysis indicated that the cobalt aluminate (spinel) is present in the residue obtained after leaching the nitric acid residue with aqua-regia solution. Visual observation indicated that blue solid slurry was readily formed during the leaching of the nitric acid residue with aqua-regia solution. This blue residue may possibly be ascribed to the presence of cobalt aluminate (spinel), which was formed during the calcination of spent catalyst at elevated temperature. Hiner (1979) and Donaldson (2001) reported that the cobaltite (cobalt aluminate), which is blue in colour, is slightly soluble in acid solution. This cobalt aluminate could be used in the ceramics and paints industries depending on its chemical purity. It could also be used as a catalyst precursor (Donaldson, 2001).

Table 3.9: Composition of residue obtained after leaching nitric acid residue with aqua-regia solution

Substance	Mass Percentage (m/m)
Fe_3O_4	1,38
MnO	0.06
Cr_2O_3	0,26
V_2O_5	0,01
TiO_2	0,51
CaO	0,31
K_2O	0,02
P_2O_5	0,00
Al_2O_3	36,2
SiO_2	28,6
MgO	0,20
Na_2O	0,10
Cl	3,00
S	0,10
Co	12,4
Pt	<0,01
Mass Change (g)	15,3

3.2.9 Crystallisation of platinum from chloroplatinic acid, H_2PtCl_6

The procedure described earlier in Section 2.2.10 was followed in order to selectively precipitate platinum species from the chloroplatinic acid. Visual observation indicated that a deep-yellow precipitate was readily formed during the addition of ammonium chloride to the chloroplatinic acid solution. Renner (2001) also found that the colour of the precipitate formed during the precipitation of platinum with ammonium chloride is deep yellow. From Figure 3.7 it can be seen that diammoniumhexachloroplatinate, $(NH_4)_2PtCl_6$ is contained in the deep-

yellow precipitate formed during the addition of ammonium chloride to the chloroplatinic acid.

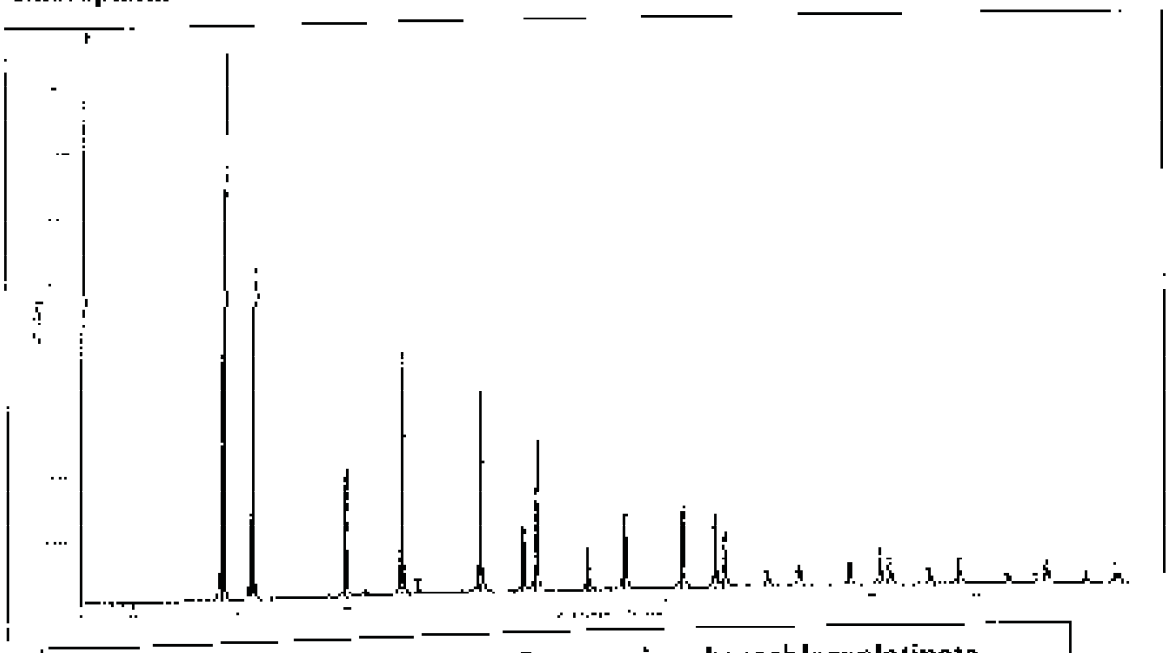


Figure 3.7: Diffraction pattern of ammonium hexachloroplatinate

* 07-0218 (*) – Ammonium platinum chloride - $(NH_4)_2PtCl_6$

The XRF results on diammoniumhexachloroplatinate originating from the spent catalyst are presented in Table 3.10 below.

Table 3.10: Composition of diammoniumhexachloroplatinate produced through the sodium-nitric acid leaching process

Substance	Mass Percentage (m/m)
Fe_2O_3	0,44
MnO	0,00
Cr_2O_3	0,04
V_2O_5	0,00
TiO_2	0,03
CaO	0,09
K_2O	0,07
P_2O_5	0,11
Al_2O_3	5,10
SiO_2	0,50
MgO	0,00
Na_2O	0,00
Cl	22,5
S	0,70
Co	0,80
Pt	46,1

It can be seen from Table 3.10 that diammoniumhexachloroplatinate co-precipitated with trace amounts of various impurities such as Fe, Cr, Ti, Ca, K, P, Si, S and Co. Approximately 5,10 % alumina is still contained in the latter and in order to further improve the chemical purity of this platinum salt, redissolution and recrystallisation of the platinum salt should be thoroughly investigated. The filtrate produced during filtration contains mostly hydrochloric acid and could be re-used in the aqua-regia solution preparation. From the afore-mentioned results obtained when using the sodium hydroxide-nitric acid leaching, it can be seen that the platinum salt was successfully recovered from the spent catalyst. This product could be converted into a platinum sponge, which may possibly be used in the new catalyst preparation for the FT process and also for the production of platinum chemicals.

3.2.10 Calcination of diammoniumhexachloroplatinate

The procedure described earlier in Section 2.2.11 was followed in order to reduce platinum(IV) ions present in diammoniumhexachloroplatinate to the platinum metal. Following the calcination of a deep-yellow diammonium hexachloroplatinate at elevated temperature, a black product was formed and the XRD analysis indicated that platinum metal is present (Figure 3.8). Habashi (1970), Hiner (1979) and Bachmann and Renner (1984) also found that on heating diammonium hexachloroplatinate, the salt decomposed to yield a platinum sponge (also termed platinum black). This product could be used as a catalyst and also for the production of platinum chemicals. Ammonia and hydrochloric acid vapours produced during calcination should be recovered and recycled to the ammonium chloride preparation step.

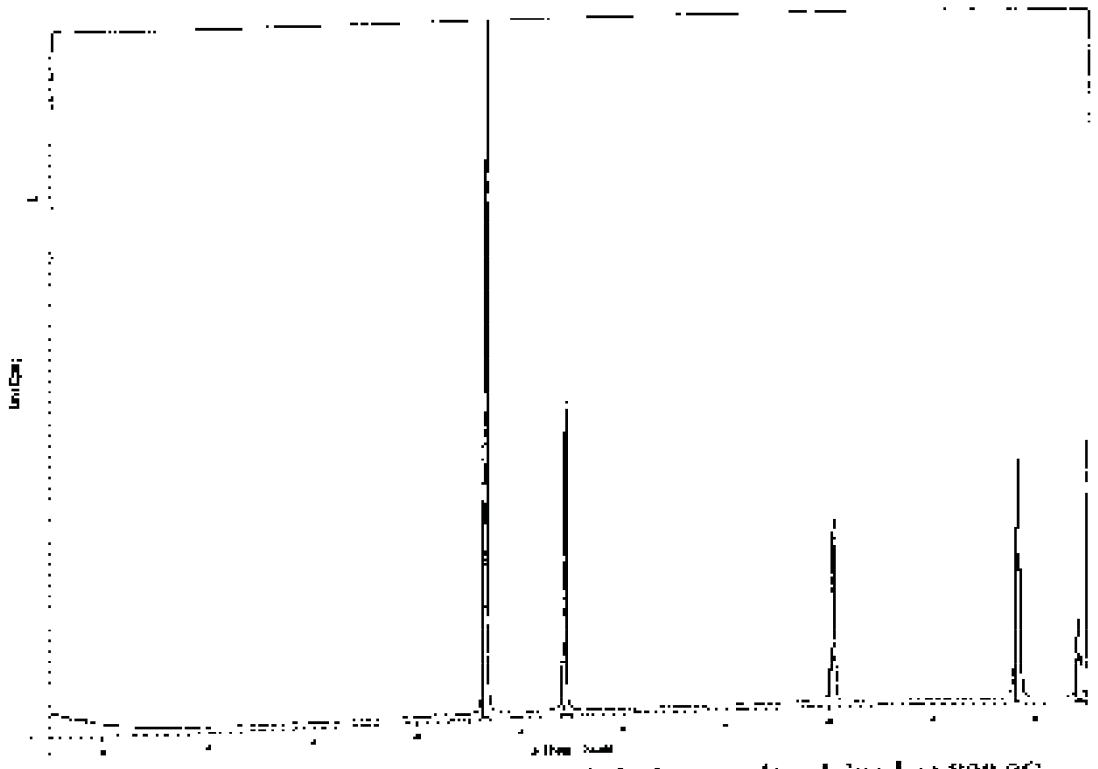


Figure 3.8: Diffraction pattern of platinum salt calcined at 800 °C

3.2.11 Precipitation of iron and aluminium from the acidic leach liquor solution

In order to prevent the loading of iron and aluminium species into an organic phase during the solvent extraction step, the precipitation of both Fe(III) and Al(III) ions from the impure cobalt containing solution should firstly be conducted. According to Appanaiian, et al (1991) the removal of the significant levels of various impurities will render solvent extraction highly efficient in the recovery of base/precious metals from the leach liquor solution. It was mentioned that the removal of the impurities prior to the solvent extraction would also further improve the selectivity of extraction. the desired metal ions from the leach liquor solution and eventually ensure a sufficiently high degree of purity in the final product.

The experimental procedure described earlier in Paragraph 2.2.12 was used to selectively precipitate iron and aluminium species from the acidic leach liquor solution. The results are presented in Table 3.11 where it can be clearly seen that the precipitation efficiency of the metal ions increase with an increase in the pH value of the impure cobalt-containing solution. The results also indicated that almost all of the Fe(III) and Al(III) ions present in the solution were successfully precipitated at pH=5.0 at 50 °C. These results are in agreement with those previously reported by Jackson (1986). It was further demonstrated that the solubility product values of metals at room temperature and the pH of the solution play an important role during the precipitation of different metal ions from the leach liquor solution in the form of metal hydroxides. It was further mentioned that Fe(III) and Al(III) ions present in nitric acid solution precipitate selectively at various pH values (in the range of 2 - 6). Co(II) ions commence to precipitate only at a pH between 6 and 12.

3.2.11 Precipitation of iron and aluminium from the acidic leach liquor solution

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Table 3.11: The precipitation efficiency of metal ions at various pH values using ammonium hydroxide solution

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	98,7	97,4
5	28,4	89,3	98,1	97,0

It can be concluded from Table 3.11 that the selective precipitation of iron and aluminium species from the impure cobalt-containing solution was successful.

3.2.12 Purification of the filtrate produced during the precipitation step through solvent extraction

The original aqueous filtrate from the precipitation step typically contains mostly Co^{2+}, NH_4^+ and NO_3^- ions and trace amounts of Pt^{2+}, Al^{3+} and Fe^{3+} ions. Habashi (1970); Jackson (1986); Ritcey and Ashbrook (1979) and Flett (1978) pointed out that solvent extraction can be used in order to selectively separate Co^{2+} ions from the leach liquor solution. In this method a suitable type of acidic extractant is used for example as an ammonium salt at a pH value between 4 and 5. This will assist in keeping the pH of the mixture relatively constant after contacting the acidic filtrate with the organic phase (containing mainly Co(II) ions). In this step, the loaded organic phase is contacted with a solution of the stripping agent (nitric acid solution) to remove the Co^{2+} species.

The experimental procedure described earlier in Section 2.2.13 was used in order to selectively extract cobalt(II) ions from the leach liquor solution. Visual observation indicated that no emulsion or third phase formation was experienced

during the solvent extraction step. In addition, the phase separation was acceptable for all tests conducted. This implies that tributylphosphate which was used as a modifier during the preparation of the organic phase, may possibly prevent the formation of an emulsion. This modifier is definitely suitable for this purpose. An important point to note is that the colour of the mixture (organic phase and aqueous phase) turned to pink at low temperature (in the range 30 - 45 °C) during the solvent extraction experiment. However, at a temperature ranging from 50 - 90 °C its colour changed from pink to blue. According to Flett, (1978) the pink colour indicates the presence of the octahedral cobalt complex in the mixture, whilst the blue indicates the 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. Subsequent to 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. This can possibly be ascribed to the absence of water in the organic phase that may otherwise form a complex with cobalt(II) ions.

The results are presented in Table 3.12 below. From Table 3.12, it is apparent that almost all of Co(II) and Al(III) ions present in the original aqueous filtrate were extracted into the organic phase during the solvent extraction. In addition, all Fe(II) ions present in the original aqueous filtrate were also loaded into the organic phase at an original aqueous filtrate: organic phase ratio of 1:8 during the solvent extraction method. It is also interesting to note that only 52 % of the iron species present in the original aqueous filtrate were extracted by the organic phase. These extracted iron species are in the +3 oxidation state. Phillips and Wills (1982) pointed out that the Fe(II) ions are not extracted by organic phase containing di-2-ethylhexyl phosphoric acid under the conditions described in Section 2.2.13.

Table 3.12: 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	82.0

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

Following the stripping of the loaded organic phase with nitric acid, the colour of the loaded organic phase (blue) turned to its original colour (colourless). This implies that the loaded cobalt species were successfully stripped from the loaded organic phase by nitric acid solution. The ICP analysis confirmed that all cobalt species loaded in the organic phase during the solvent extraction method are contained in the purified leach liquor solution. The stripped organic phase could be recycled to the solvent extraction step.

3.2.13 Crystallisation of the cobalt nitrate from the leach liquor solution

Habashi (1970) pointed out that crystallisation of metallic salts from the leach liquor solution depends strongly on the temperature, organic solvents and complexing agents. It was further stated that as the temperature of the leach liquor solution is increased to 100 °C the solubility of the metals decreases. Finally the precipitation of crystals takes place. Subsequent to the concentration of the cobalt nitrate-containing leach liquor solution by evaporation, the resulting leach liquor

solution as well as the purified leach liquor is crystallised to form a red-brown crystalline cobalt nitrate salt ($Co(NO_3)_2 6H_2O$ (Donaldson, 2001). This salt is currently used in the production of high purity cobalt and also in the electronics and chemical industries. Furthermore, it could possibly be used in the Fischer-Tropsch reaction for the industrial synthesis of certain hydrocarbons from carbon monoxide and hydrogen. The filtrate containing free water and nitric acid would be utilised in the crystallisation step to obtain cobalt nitrate.

The experimental procedure described earlier in Section 2.2.14 was followed in order to crystallise cobalt nitrate from the purified leach liquor solution. The results are presented in Table 3.13 below. Visual observation indicated that red-brown crystals were formed after cooling the concentrated leach liquor solution to room temperature. The XRD analysis showed that cobalt nitrate is present in both Sastech and commercial cobalt nitrate samples. It is apparent from the results in Table 3.13 that the pure Sastech cobalt nitrate produced after using the solvent extraction compares more favourably to the commercial cobalt nitrate in terms of the chemical purity. The results also indicated that the concentration of cobalt in the impure cobalt nitrate crystals is very low. This may be attributed to the low retention time of the crystals during the drying step and also the low concentration of nitric acid used during the dissolution step.

Table 3.13: Composition of Sastech and commercial 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	0,03	0,03	0,03
MnO	0,03	0,04	0,04
Cr_2O_3	0,02	0,03	0,03
V_2O_5	0,01	0,01	0,01
TiO_2	0,02	0,02	0,02
CaO	0,05	0,06	0,07
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	0,00	0,00
MgO	0,00	0,00	0,00
Na_2O	0,00	0,00	0,00
Cl	0,00	0,00	0,00
Pt	0,000074	0,00066	0,0003
Co	22,8	16,3	20,0

The crystallisation of cobalt nitrate from the leach liquor solution produced from the dissolution step was proved to be successful. This compound may in future be used in the new catalyst preparation step for application in the Fischer-Tropsch reaction.

In order to increase the concentration of cobalt in the impure cobalt nitrate crystals, the retention time of the crystal at 55 °C should 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.

3.2.14 Crystallisation of aluminium trihydrate (ATH) from sodium aluminate solution

The experimental procedure described earlier in Section 2.2.14 was followed in order to crystallise aluminium trihydrate from sodium aluminate solution. The results obtained are presented in Table 3.14 and graphically depicted in Figures 3.8 and 3.9. Visual observation indicated that white crystals were readily formed during the storing of sodium aluminate solution in a container for a one-month period. The XRD analysis indicated that gibbsite ($Al(OH)_3$) is present in commercial aluminium trihydrate and white crystals produced during crystallisation of aluminium trihydrate from sodium aluminate solution. The ICP results also indicated that approximately 99 % of the Al present in the sodium aluminate solution crystallised in the form of the gibbsite. Overall, the elemental analysis indicated that aluminium trihydrate with a chemical purity of 99 % was produced after the crystallisation step.

From Table 3.14, it can also be seen that aluminium trihydrate produced during the crystallisation step crystallised with 0,11 % CaO and 0,7 % Na_2O. The presence of calcium oxide in the crystals could be ascribed to the use of calcination equipment, which was contaminated with calcium oxide sources. However the presence of sodium oxide in the crystals may be attributed to the sodium aluminate solution retained during filtration. To reduce the concentration of sodium oxide present in the crystals, water-washing technique should be included in the process of recovering high value metals from the spent catalyst. ICP analysis indicated that about 20 % w/w NaOH was contained in the filtrate recovered during the filtration of the aluminium trihydrate slurry. Eventually, this filtrate can be recycled to the sodium hydroxide leaching step where it is utilized as a lixiviant.

The PSD (particle size distribution) results are presented in Table 3.15 where it can be seen that aluminium hydroxide originating from the spent catalyst consists

of ultra-fine solid particles (72.9 % of material passed a 10 µm sieve). The commercial aluminium hydroxide, which is being produced by Kynochem, contains coarse particles (2 % of the material passed a 10 µm sieve). The presence of the additional ultra-fine solid particles in aluminium hydroxide emanating from the spent catalyst may possibly be attributed to the absence of crystal seeds during the crystallisation of aluminium trihydrate. To further improve the rate of aluminium trihydrate crystallisation and reduce the amount of small particles during crystallisation, a saturated sodium aluminate solution should be seeded with a commercial aluminium trihydrate. Genck (1993) stated that in practice, the batch may be self-nucleated or seeded.

From Table 3.14 it follows that the product produced during crystallisation of the aluminium trihydrate from sodium aluminate complies favourably with the specification of aluminium trihydrate that is currently produced by Kynochem. Aluminium trihydrate is commercially used as a raw material for the production of aluminium chemicals such as aluminium sulphate, aluminium chloride, sodium aluminate and alumina. It can also be used as a catalyst support.

Table 3.14: Composition of Sastech aluminium trihydrate and the commercial aluminium tribydrate

Substance	Commercial ATH Mass percentage w/w	Sastech ATH Mass percentage w/w
Fe_2O_3	<0,2	0,0
MnO	<5ppm	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
As	5ppm	3ppm
Cu	5ppm	0,0
Pb	5ppm	6ppm
Se	5ppm	0,0
Cd	<1ppm	0,0
Zn	<0,1%	19ppm
F	<0,1%	65ppm
Hg	<1ppm	<10ppb
NO_3	<0,1%	N.D
NO_2	<0,1%	N.D
CN	<5ppm	N.D
Co	17ppm	15ppm
Pt	<1ppm	<1ppm
Mass Change (LOI)	- 35%	-34,9%

Table 3.15: PSD analysis of commercial aluminium hydroxide and aluminium hydroxide from the spent catalyst

Sieve Diameter (µm)	Commercial aluminium hydroxide (Percentage passing)	Aluminium hydroxide from spent catalyst (Percentage passing)
10	2,0	72,9
20	4,6	97,2
30	13,2	99,6
50	20,2	100

3.2.15 Calcination of aluminium trihydrate to form alumina

In an attempt to produce alumina suitable for the Fischer-Tropsch catalyst, aluminium trihydrate produced during the crystallisation step was calcined at various temperatures (ranging from 400 – 600 °C) in the presence of air. Following the calcination step, a white powdered product was formed. Subsequently, both product and Condea Chemie alumina (currently used in the catalytic reaction as a supporting material) were submitted for XRD, surface area, and pore volume analysis

The XRD analysis indicated that boehmite was formed at 400 °C while gamma was formed at 600 °C during the calcination of Sastech aluminium trihydrate (see Figures 3.9 and 3.10). Gamma-alumina was also present in the Condea Chemie sample. From these XRD results it could be concluded that phase transformation during the calcination step is temperature dependent.

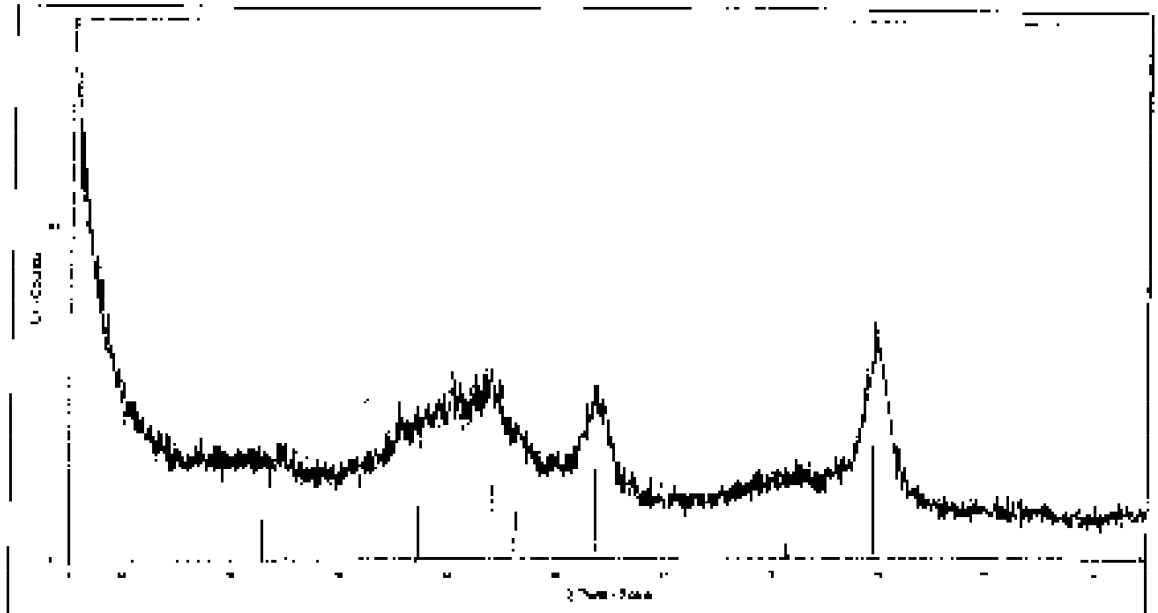


Figure 3.9: Diffraction pattern of aluminium trihydrate calcined at 600 degC for 1 h
29-0063 (N) – gamma-Aluminium Oxide – Al2O3

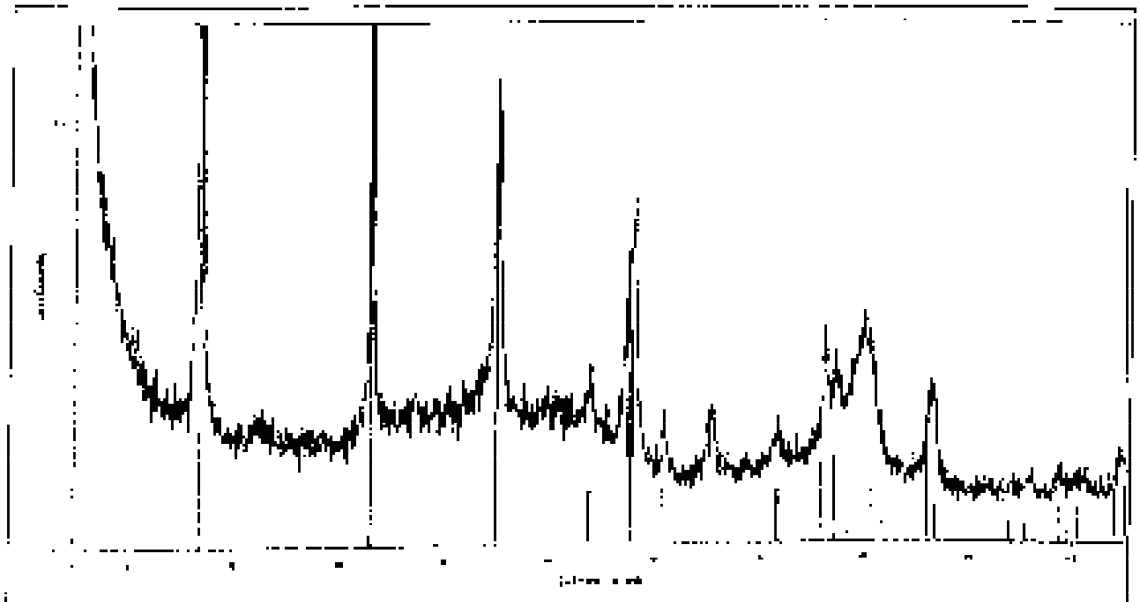


Figure 3.10: Diffraction pattern of aluminium trihydrate calcined at 400 degC for 1 h
21-1307 (I) – Boehmite, syn 0 AlO(OH)

From Table 3.16, it can seen that Sasteeh R&D alumina originating from spent catalyst outperformed an alumina which is being produced by Condea Chemie in terms of the surface area. The pore volume of Sasteeh R&D alumina is however much lower than that of the Condea Chemie alumina. A support with high surface area and pore volume is required to allow the active sites of the catalyst to develop and disperse evenly during the manufacture process.

Table 3.16: Surface area and pore volume measurements of Condea Chemie alumina and alumina from spent catalyst

Samples	Surface area (m^2/g)	Pore volume (ml/g)
Condea chemie alumina	150,0	0,45
Sasteeh R&D alumina	180.5	0.29

3.2.16 Preparation of catalyst

As stated previously in Chapter 1, the products formed during the envisaged process of recovering high value metals from the spent catalyst could be recycled to the new catalyst preparation step. The cobalt catalyst produced during the proposed process could be useful for conducting carbon monoxide hydrogenation reactions, particularly Fischer-Tropsch reactions.

The experimental analytical methods and procedure described earlier in Sections 2.2 and 2.2.17 were followed in order to prepare and characterise the cobalt-based catalyst. The results obtained during the application of the aforesaid methods were presented and discussed as follows:

3.2.16.1 The elemental analysis

The results obtained on the cobalt-based catalyst emanating from the spent catalyst derived-impure cobalt nitrate/pure cobalt nitrate and commercial cobalt nitrate are presented in Tables 3.17, 3.18, 3.19, 3.20 and 3.21 below.

Table 3.17: Composition of catalyst prepared by impregnating alumina with Sastech pure cobalt nitrate in the furnace

Substance	Mass Percentage (m/m)
Fe_2O_3	1,31
MnO	0.08
Cr_2O_3	0.04
V_2O_5	0.01
TiO_2	0,10
CaO	0,22
K_2O	0.03
P_2O_5	0.06
Al_2O_3	70,6
SiO_2	0,40
MgO	0,00
Na_2O	0,50
Cl	0,01
S	0,10
Co	14.6
Pt	0,000627
Mass Change (g)	6,45

Table 3.18: Composition of catalyst prepared by impregnating alumina with commercial cobalt nitrate calcined in the furnace

Substance	Mass Percentage (m/m)
Fe_2O_3	0,59
MnO	0,06
Cr_2O_3	0.03
V_2O_5	0.00
TiO_2	0,04
CaO	0,08
K_2O	0.00
P_2O_5	0,00
Al_2O_3	64,6
SiO_2	0,10
MgO	0,00
Na_2O	0,10
Cl	0,00
S	0,10
Co	20,2
Pt	0,000532
Mass Change (g)	6,67

Table 3.19: Composition of catalyst prepared by impregnating alumina with impure cobalt nitrate calcined in the calcination tube

Substance	Mass Percentage (m/m)
Fe_2O_3	0,62
MnO	0,05
Cr_2O_3	0.03
V_2O_5	0,00
TiO_2	0,01
CaO	0,06
K_2O	0,00
P_2O_5	0,00
Al_2O_3	76,1
SiO_2	0,00
MgO	0,00
Na_2O	1,50
Cl	0,00
S	0,10
Co	9,45
Pt	0,0662
Mass Change (g)	7,79