THE SELECTIVE DISSOLUTION AND RECOVERY OF HIGH VALUE METALS FROM SASOL PROPRIETARY SPENT COBALT-BASED CATALYST AND SUBSEQUENT CHARACTERISATION OF THE PRODUCTS FORMED.

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DECLARATION

I, Ratale Henry Matjie declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

Henry Matjie

Name of candidate

23rd day of August 2002

ABSTRACT

The cobalt catalyst supported on alumina catalyses the FT-reaction to produce hydrocarbons and oxygenated hydrocarbons from syngas. The deactivated catalyst from the FT-process is subsequently being discarded as spent catalyst. This study describes the selective recovery of alumina, cobalt and platinum from the spent catalyst prior to its disposal of.

The unique process developed comprises the following steps: Calcination, NaOH and nitric acid leaching, Precipitation, Solvent extraction, Crystallisation and Flocculation. The effects of the leaching parameters on the metal extraction efficiencies from the calcined spent catalyst were investigated.

Results indicated that the leaching parameters evaluated have significant effects on the metal extraction efficiencies. Hydrometallurgical purification methods utilised in this study were effective

The products from the proposed process were used to prepare a FT-catalyst and was subsequently characterised by physio-chemical techniques. The characterisation results on the spent catalyst derived products compared favourably to those of the commercial catalyst.

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LIST OF ABBREVIATIONS

Å	Armstrong
ATH	Alumina trihydrate
AECI	African Explosives Chemicals Industries
atm	atmosphere
Bar	unit of pressure equal to 10^6 dynes per square centimetre
BET	Brunauer Emmett Teller
C^*	Equilibrium Solubility
CSD	Crystal Size Distribution
DSC	Differential Scanning Calorimetry
D2-EHPA	Di-2-ethylhexylphosphoric acid
Floes	flocculated solids
FT	Fischer-Tropsch
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
IX	Ion-Exchange
LOI	Loss On Ignition
µm	microns
Natref	National Petroleum Refiners of South Africa (Pty) Limited
NTU	Nephelometric Turbidity Units
ppm	parts per million
PSD	Particle Size Distribution

σ	Relative supersaturation
rpm	revolution per minute
Sasol	South African Coal, Oil and Gas Corporation
Sastech R&D	Sasol Technology Research and Development
SCI	Sasol Chemicals Industries
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SMX	Sasol Mining Explosives
STP	Standard Temperature and Pressure
SX	Solvent Extraction
TBP	Tributylphosphate
TPR	Temperature Programmed Reduction
Vol	volume
XRD	X-Ray Diffraction
XRF	X-Ray fluorescence
XPS	X-ray Photoelectron Spectroscopy

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CHAPTER 1

INTRODUCTION

1.1 General introduction

The Sasol group of companies is currently using the Fischer-Tropsch process to produce hydrocarbons from synthesis gas. Synthesis gas (also referred to as syngas) is a mixture of carbon monoxide and hydrogen produced via the gasification of coal. The Fischer-Tropsch process is named after Franz Fischer and Hans Tropsch who discovered the process in 1923 when they contacted syngas with an iron catalyst at elevated temperatures (Fischer and Tropsch, 1927). Subsequent studies have shown that this process can be catalysed by other transition metals, including cobalt. The catalysts utilised in this process can either be supported or unsupported. The range of supports generally used includes SiO_2, Al_2O_3, ZrO_2, TiO_2 (Storch, et al 1951). The Fischer-Tropsch process is carried out at pressures above ambient in a fixed bed, slurry bed or Berty reactor.

The Sasol cobalt based FT process is carried out in a slurry phase reactor using an alumina-supported catalyst. The catalyst is promoted with minute amounts of platinum, which is believed to be a reduction promoter. The aluminium oxide support is produced by Sasol Chemie (formerly known as Condea) and the metal precursors, cobalt nitrate and tetraamine Pt(II) nitrate, are obtained from other commercial vendors. The cobalt-based catalyst deactivates with time on stream and the loss in activity is attributed to sulphur poisoning and coke formation.

Hydrogen sulphide and thiols that are formed during the gasification of coal are implicated as the sources of sulphur present in the syngas feed. The spent catalyst arising from the Sasol cobalt-based Fischer-Tropsch process typically contains carbonaceous material (60 - 70 %), cobalt oxide (8 - 10 %), platinum (0.01 - 0.02 %) and aluminium oxide (20 - 27 %).

The high costs of the precursor metal salts coupled with the toxicity of cobalt and platinum render the disposal of the spent catalyst uneconomic and unacceptable. An alternative option involving the recovery of these metals from spent FT catalyst has therefore been considered. Several methods used to recover metals from spent catalysts have been developed and these are described in the following section.

1.2 Literature survey

According to the literature the most commonly used method to selectively recover metals from the spent catalyst prior to its disposal is the multi step metallurgical procedure described below. This method entails:

- Calcination of the spent catalyst
- Selective leaching of high value metals by inorganic acid and/or strong bases
- Flocculation and filtration of the slurry
- Purification of the leach liquor solution by a solvent extraction method, ion exchange resin method and subsequent selective precipitation
- Crystallisation of the metals as salts.

According to Helmboldt and co-workers (2001) the Bayer process, which involves the digestion of bauxite ore containing aluminium oxide and silicon dioxide with sodium hydroxide at relatively high temperatures ranging from 110 - 320 °C and pressure ranging from 4 - 20 Bar to form sodium aluminate, is utilized to selectively remove alumina from aluminium-containing ores. Earlier studies by Hahoshi (1970) demonstrated that alumina could be selectively and efficiently removed from spent catalysts containing heavy metals by extracting it with sodium hydroxide solution. This method leads to no substantial dissolution of heavy and base metals from the spent catalyst. Welsh et al (1981) later developed a method

to remove high value metals from spent catalysts. These researchers use the following steps:

- Calcination of the spent catalyst only in the presence of oxygen, followed by the chlorination to recover high value metals
- Acid leaching involving sulphur dioxide, sulphuric acid and hydrochloric acid
- Filtration
- Disposal of the catalyst support
- Transportation of high value metal oxide products to a refinery.

It should be mentioned that the method used by Welsh and co-workers does not selectively remove heavy metals from the support as it leads to dissolution of all metals present in the spent catalyst. This method is only applicable to systems containing silica as a support. The addition of sodium carbonate or sodium chloride to the spent catalyst containing organic material prior to calcination (to selectively remove alumina) on sulphur removal and the undesired formation of cobalt aluminate (spinel) was not investigated by Welsh. This step would also assist in converting water insoluble aluminium oxide to a water-soluble compound (sodium aluminate or silicate).

Thus far, reports on parameters affecting the separation efficiency of base insoluble residues containing mainly cobalt and platinum species are lacking. This could be attributed to the difficulty in separating the two. However, it is envisaged that a process including the following steps could alleviate this problem:

- Calcination
- Base-leaching
- Flocculation and filtration
- Selective precipitation
- Selective dissolution of cobalt from the basic residue with a solution of nitric acid

- Flocculation and filtration
- Precipitation of impurities prior to the applicable of a solvent extraction procedure
- Solvent extraction
- Crystallisation of impure and purified cobalt nitrate from the leach liquor solution
- Dissolution of platinum from the nitric acid residue by means of formation of an aqua-regia solution
- Crystallisation of a platinum salt.

This dissertation deals only with the above-mentioned steps of the envisaged process. These steps are discussed in detail in the following section.

1.2.1 Calcination

As stated in section 1.1 above, the spent catalyst typically contains 60 - 70 % carbonaceous materials, 8 - 10 % cobalt and 20 - 27 % alumina. The primary role of a calcination and sintering step is to oxidise the carbonaceous materials present in the spent catalyst prior to either acid or base leaching. According to Hubred and Van Leirsburg (1984), Toida et al (1979) and Toyabe et al (1995b), spent catalyst is firstly calcined at a temperature ranging from 600 - 1000 °C in order to oxidise carbonaceous materials present in the spent catalyst prior to the leaching step. Toida et al (1979) and Burnet et al (1984) clearly stated that sodium carbonate and sodium chloride can react with alumina when sintering at a temperature ranging from 600 - 950 °C to form a sodium aluminate. This compound can rapidly dissolve in water or in a solution of alkali hydroxide such as sodium hydroxide or potassium hydroxide. The following reaction occurs during the sintering or calcination of a mixture of sodium carbonate/ chloride and spent catalyst:

$$\underset{\text{alumina}}{Al_2O_{3(s)}} + Na_2O_{(s)} \rightarrow \underset{\text{sodium aluminate}}{NaAlO_{2(s)}} \qquad (1.1)$$

The resulting calcined spent catalyst with no carbonaceous materials will eventually be used in the leaching step to recover high value metals. The demerit of calcination to remove carbonaceous material is that the high temperatures used could also enhance the formation of cobalt aluminate, which dissolves with difficulty in a solution of sodium hydroxide or nitric acid.

1.2.2 Leaching of the spent catalyst

For purposes of further discussion, leaching is considered as the process of dissolving high value metals with a solution of acid or base from either calcined ores, residues, scrap or spent catalysts. Jackson (1986) clearly stated that the leaching step yields a leach liquor solution that is rich in metal ions. These metal ions can be selectively separated through a purification method. Burnet et al (1984), Canon et al (1979), Welsh et al (1981), Toida et al (1979), Wiewiorowski (1987), Sebenik (1985) and Toyabe et al (1995a) use two types of hydrothermal leaching processes to enhance recovery of high value metals from spent catalyst and coal ash. The hydrothermal leaching processes, namely alkaline and acid will briefly be described in the following sections.

According to Jackson (1986) the leaching of an oxide may involve one of the three types of reactions: chemical dissolution, oxidative dissolution and reductive dissolution. This author also reported that chemical dissolution involves the reactions between several of metallic oxides and either inorganic acids such as sulphuric acid and nitric acid or strong alkali hydroxide base such as sodium hydroxide. It was further suggested that it should be possible to chemically dissolve bauxite ore (essentially alumina-bearing ore) in either acidic or alkaline media. Under such conditions, the following reactions occur respectively:

$$Al_2O_3 + 6H^+ = 2Al^{3+} + 3H_2O \qquad (1.2)$$

$$Al_2O_3 + OH^- \quad 2AlO_2^- + H^+ \qquad (1.3)$$

These two possible reactions are still being used almost exclusively for the extraction of aluminium from the oxidised ores by either sulphuric acid or sodium hydroxide pressure leaching processes. The pH dependence of these extraction processes is schematically shown in Figure 1.1 below.

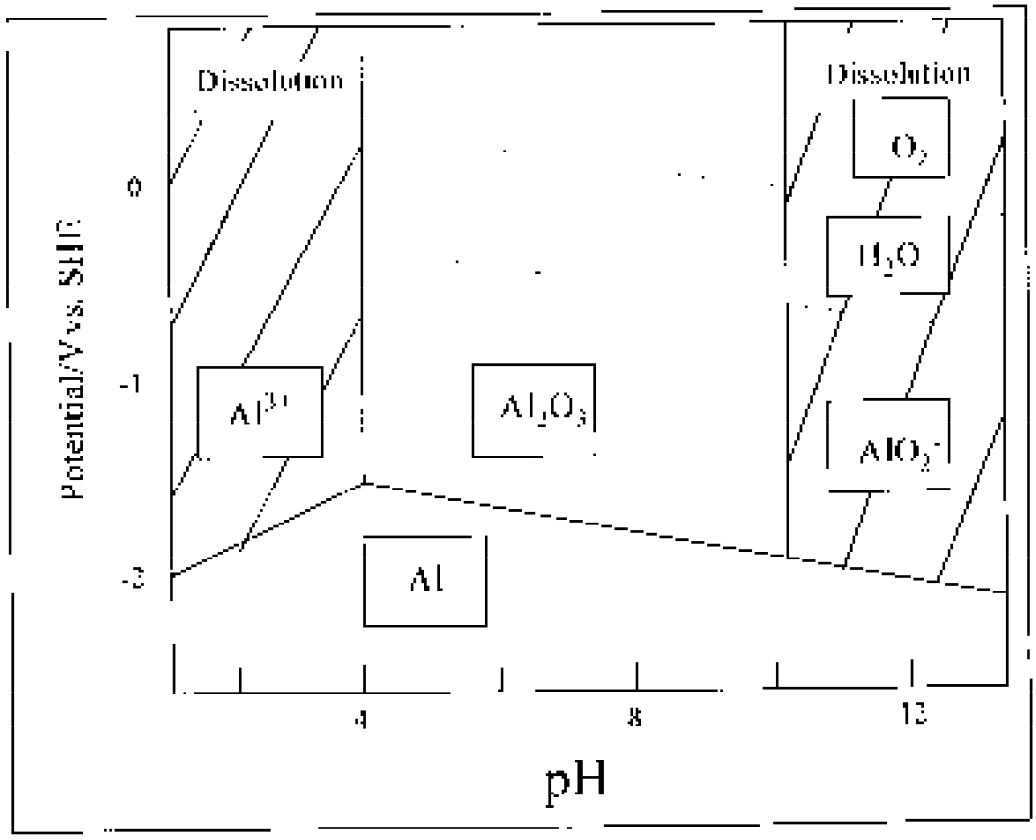

Figure 1.1: Potential/pH diagram for the aluminium-water system (for a metal ion activity of 10^{-4} mol kg^{-1} at 25 °C)

It is further reported that the direct chemical dissolution in a non-oxidising acid does not occur very readily. When a non-oxidising acid is used to effect oxidative leaching, iron(III) salts or other oxidising agents are usually added to the leaching medium. According to Jackson (1986) reductive dissolution of other oxides is impractical.

Jackson (1986) used the model of the dissolution process of a metal oxide postulated by Warren Devuyst to dissolve metal oxide in a dilute, non-oxidising acid. Jackson (1986) argued that during the dissolution process a complexing anion results in the formation of a soluble aquo-cation. This model assumes that the areas of dissolution on the surface of the oxide are likely to be those sites that have higher chemical energy, such as certain planes, edge dislocations and other areas of atomic disarray. Lower activation energies will be associated with the reaction.

Jackson (1986) also found that the dissolution of metal oxide in aqueous acids depends on the anisotropy of the solid. Selected sites of the oxidised solid firstly prefer the intake of water molecules and surface hydroxylation occurs. This step might be rate determining for some oxidised solids under certain conditions. However, the subsequent protonation and anion adsorption steps happen rapidly and result in desorption of a metal-containing species. Water can therefore react with the metal containing species to form the metal aquo-cation and the corresponding anion. According to Jackson (1986) the desorption step rather than hydroxylation may play an important role in controlling the reaction rate during the dissolution process. It was further reported that the addition of a complexing agent might enhance the modification of several stages of the process, eventually resulting in the formation of a soluble reaction product. A summary of the mechanism for the dissolution of a metal oxide in aqueous acid is illustrated in Figure 1.2.

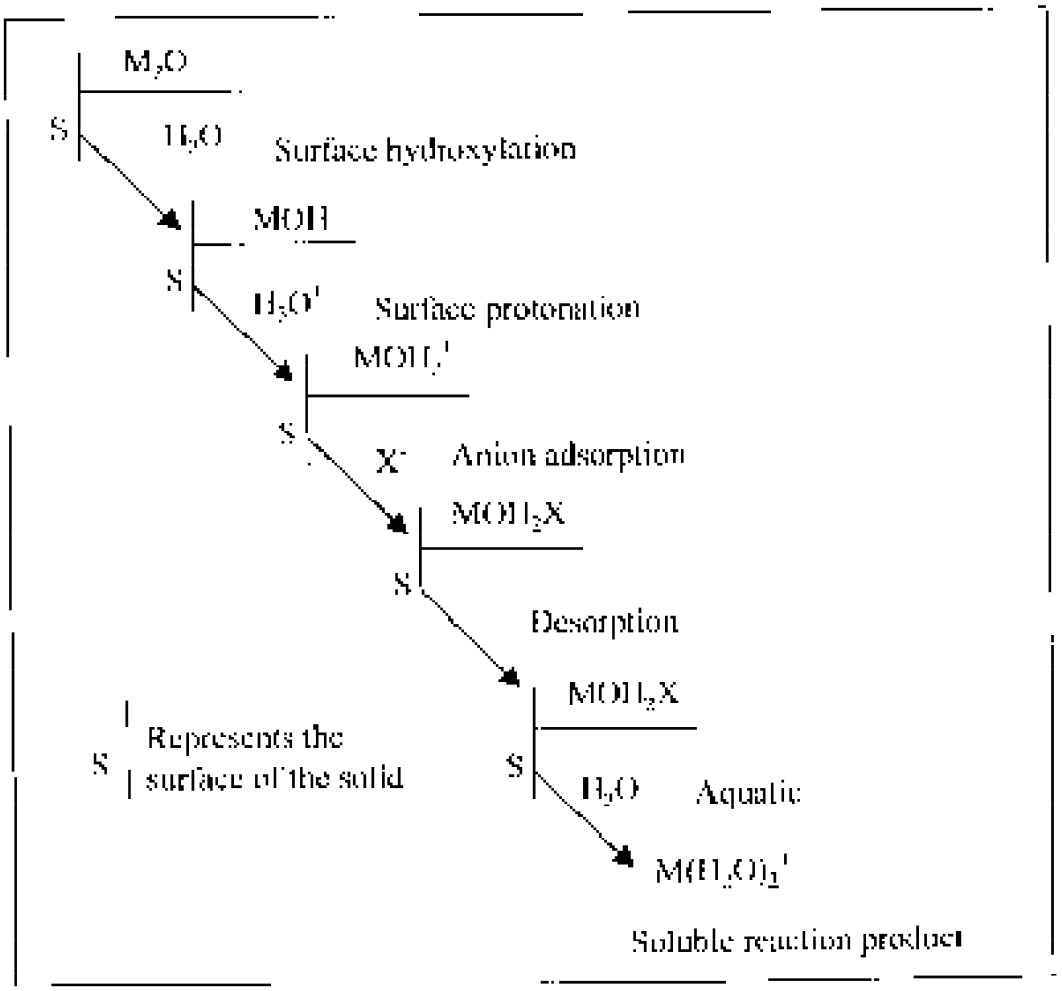

Figure1.2: Outline of the reaction-stage mechanism for the dissolution of a metal oxide in aqueous acid

1.2.2.1 Alkaline leaching process

In 1888 Karl Josef Bayer in Russia initially proposed a process of digesting bauxite in a solution of sodium hydroxide to selectively dissolve aluminium-bearing minerals from the ore. This commercial process is shown in Figure 1.3 and is currently used almost exclusively for the production of alumina, which is suitable for the subsequent production of aluminium metal.

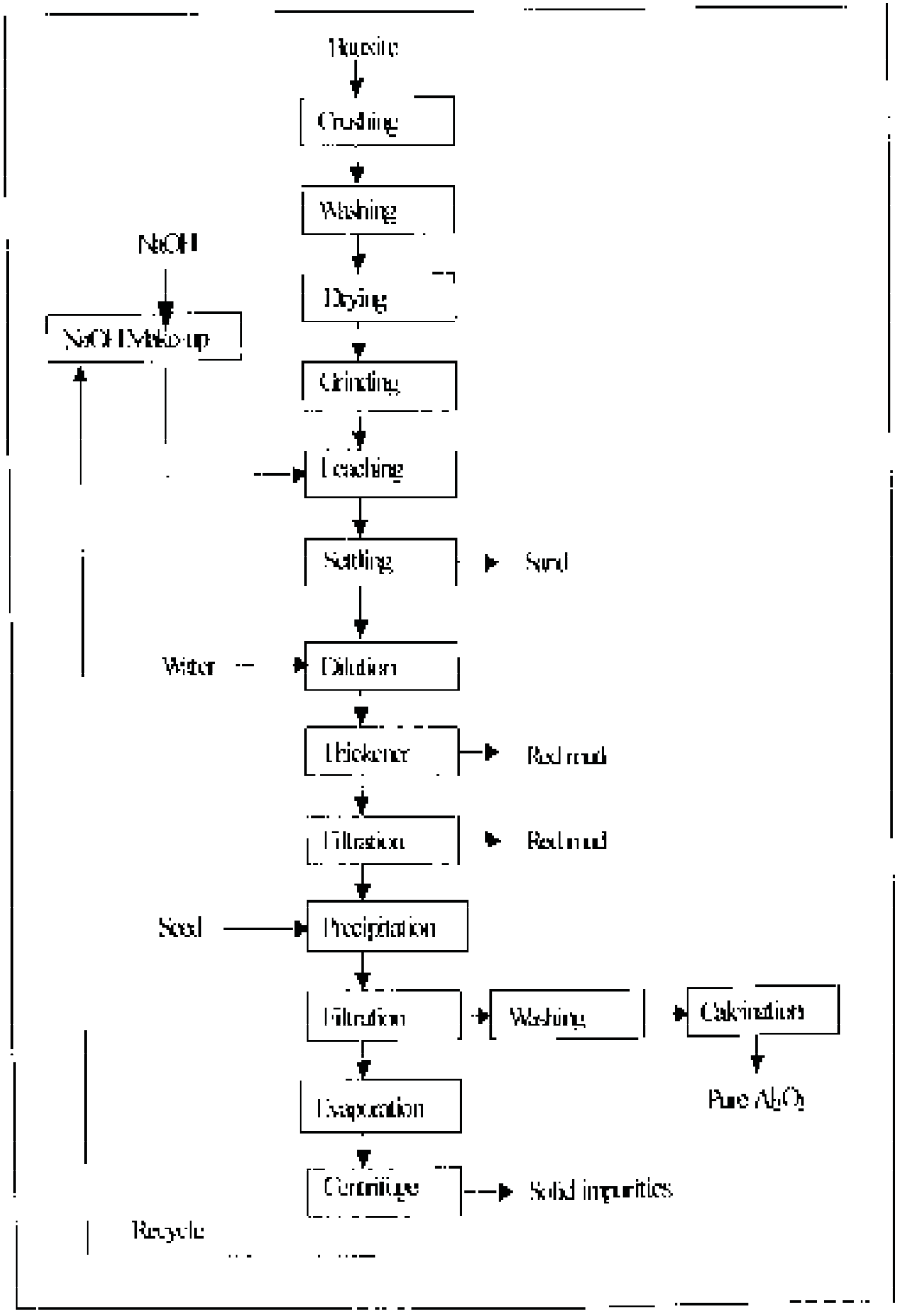

Figure 1.3: Bayer process for treating bauxite