REGENERATION OF SPENT ACTIVATED CARBON

BY

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REGENERATION OF SPENT ACTIVATED CARBON,
AT NKANA COBALT PLANT.

SUBMITTED BY
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ABSTRACT

Two methods for the regeneration of activated carbon loaded with sulphide anions and organic adsorbates have been studied on a laboratory scale and are described in this report. Activated carbon is used to reduce by adsorption the level of sulphide anions in cobalt advance electrolyte. During adsorption sulphide anions accumulate on free sites of activated carbon and as a result there is a progressive decline in activity of the carbon. After sometime, the activity drops to a level where very little adsorption takes place. This creates a need to regenerate the carbon and restore its activity. If the level of impurities is not reduced in the electrolyte, problems arise at the electrowinning stage of cobalt and also during use of cobalt metal.

The first method of carbon regeneration described in this report is that of chemical regeneration. This method involved the use of two regenerants: hydrochloric acid and a mixture of sulphuric acid and potassium dichromate. Experiments done have shown that this method is technically feasible as a regeneration efficiency of 90 and 93% for sulphuric acid and potassium dichromate and hydrochloric acid respectively was obtainable. However, a major disadvantage of the method is the high cost of regenerants.

The second method which has shown more potential than chemical regeneration is thermal regeneration. This method involves heating spent carbon to a temperature of 600 - 900 degrees celcius in an inert atmosphere. Batch experiments have indicated the technical and economic feasibility of this method. A regeneration efficiency of 93% is obtainable at a temperature of 700 degrees celcius.
CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

The current annual world production of cobalt is about 18997 tonnes [1], 22.17% of which is produced by Zambia Consolidated Copper Mines (ZCCM) at its Nkana and Chambishi Cobalt plants. Most of the cobalt produced is ultimately used in the manufacture of high strength and heat resistant alloy steels. For such applications sulphur is one of the most deleterious impurities [2], because it concentrates on grain boundaries and reduces the high temperature strength of steels. Consequently for cobalt produced by ZCCM, it is specified that the sulphur content shall be 30 ppm or less [3] (details in Appendix 1).

In addition to the problem noted above which the end-user of cobalt metal would face, high sulphur also poses a problem in the production process at the electrowinning stage. The dominant process for the production of cobalt, the Roast - Leach - Electrowon route, will be described in a subsequent section (Section 1.3). A high sulphur content in the electrolyte (in the form of \(S^{2-}\)) causes some evolution of \(H_2S\) gas at the stainless steel cathode blanks [2]. This gas forces cobalt metal being deposited by the main cathode reaction to "peel" off the cathode and warp outwards. The most serious drawback of such peeling off of cobalt from the cathodes is that it results in short circuits as anodes and cathodes make contact. This drastically reduces current efficiencies and hence tremendously increases production costs. The anode - cathode contact also results in lead contamination of the metal from the lead -antimony anodes by physical occlusion of
anode corrosion products.

At ZCCM's Nkana cobalt plant, the sulphide anion content in the solution proceeding to the tankhouse is typically 0.4 ppm. These sulphide anions originate mostly from lime which is added as a precipitant at an earlier stage in the production process. Before cobalt electrowinning is conducted, the sulphide anions are reduced to less than 0.14 ppm in the solution entering the tankhouse as electrolyte. This is achieved by passing the high sulphide anion containing solution through a column of activated carbon. Some of the sulphide anions are adsorbed onto the carbon, thus resulting in a solution with a low sulphide content to exit the column. This solution enters the tankhouse as electrolyte. In addition to adsorbing sulphide anions, activated carbon also removes by the same mechanism, organic species present in solution such as residual flocculants originating from upstream processes. Removal of organics from the solution entering the tankhouse as electrolyte is beneficial as such organics would otherwise be partly entrapped in the cobalt metal depositing on the cathode thus contaminating it. With continued passage of the cobalt solution through the activated carbon column, the number of active sites on the carbon progressively decreases due to the sulphide anions and organics being adsorbed. The ability of the column to remove sulphide anions and organic impurities thus decreases with time.

At the Nkana cobalt plant, once activity of carbon has dropped to less than 50% of that of fresh carbon, some of the lost activity is restored by passing a mixture of 100 gpl \( \text{H}_2\text{SO}_4 \) and 2 gpl \( \text{K}_2\text{Cr}_2\text{O}_7 \) through the column. Most of the sulphide anions and organics adsorbed on the carbon are desorbed and diffuse into the flowing acid which later exits the carbon column as a waste product. Total regeneration of the carbon is as a rule
not possible. This is due to some loss of porosity brought about by physical degradation of carbon granules and the filling-up of some carbon macropores with residual fine solids not removed by clarification in earlier process steps. The extent of carbon regeneration is also dependent on the suitability of the regenerant to remove the adsorbed species, some of which are more tenaciously held than others. As a result of the unregenerable sites on the carbon granules, a time comes when the total number of active sites on the carbon drops to an unacceptably low value. Once this happens the spent carbon is discarded and the column is loaded with fresh activated carbon.

At Nkana cobalt plant, when the activated carbon in the column is new, within-column regeneration is done once every month or so. With passage of time and progressive increase of unregenerable sites, regeneration has to be done more frequently. After about 13 months the carbon is virtually unregenerable and has to be discarded, and fresh carbon is put into the column.

1.2 OBJECTIVES OF THE PROJECT.

The project whose results are presented in this report was concerned with the regeneration of activated carbon. The objectives of the project were two fold. Firstly it was required to assess the ability of a thermal method for regenerating spent activated carbon. The other objective of the project was to determine the suitability of using a mixture of sulphuric acid and potassium dichromate and alternatively hydrochloric acid for regeneration of spent activated carbon. It was also required to compare the efficiency of the two regeneration methods.

The project was carried out by means of laboratory investigations at the Nkana cobalt plant during the period
November, 1993 to January, 1994. Samples of spent activated carbon for use in the experiments were obtained from a heap behind the cobalt plant where spent carbon is dumped.

1.3 DESCRIPTION OF NKANA COBALT PLANT OPERATIONS.

Cobalt concentrates arriving at the Nkana cobalt plant are obtained from three sources, namely Nkana, Nchanga and Baluba concentrators. Typical analyses of the concentrates are shown below:

<table>
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<th>Concentrate type</th>
<th>%Cu</th>
<th>%Co</th>
<th>%S</th>
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<tr>
<td>Nchanga</td>
<td>16</td>
<td>8.0</td>
<td>15.0</td>
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<tr>
<td>Baluba</td>
<td>10</td>
<td>1.8</td>
<td>30.0</td>
</tr>
<tr>
<td>Nkana</td>
<td>10</td>
<td>1.5</td>
<td>21.0</td>
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The three types of concentrates are blended to give the cobalt plant feed which has a composition of about 8 - 11% Cu, 2.5 - 3.5% Co and 22 - 26% S. Starting from the blended concentrate, the Nkana cobalt plant produces separate copper and cobalt metals using the sequence of operation shown in Figure 1.

The blended concentrate is first slurried with water to 65 - 70% solids (slurry specific gravity 1.05 - 2.05). The slurried concentrate is then pumped into a fluidized bed roaster operating at 700°C. The roasting operation converts acid insoluble copper and cobalt sulphides in the concentrates into soluble sulphate/oxide phases. The roaster off gas produced with 5 - 6% sulphur dioxide goes to Nkana acid plant for use in the production of 98% sulphuric acid. The roaster has a through-put of about 420 dry tonnes of concentrates per day when there is oxygen enrichment (oxygen enrichment is done all the time when the oxygen plant is on line). 350 dry tonnes per day is the through-put when no oxygen enrichment is used. The hot calcine at 700°C from the roaster enters a quench vessel containing acid-bearing spent copper electrolyte. The pulp
Figure 1: Simplified WKAJ Flowchart

1. Go to Metallurgical Plant
2. Vacuum Degassing
3. Crushing
4. Co Electrowinning
5. Electrolyte Preparation Stages
   - Zn
   - Fe
   - Cu Activation
   - Carbon Cleaning
   - Fe, Cu Removal
   - Fe, Cu Separation
6. Precipitation
   - pH 8.3
   - Lime
   - Cu Electro-winning
7. KO2ing
   - 70% KO2
8. Sulfuric Acid Concentrates
9. Co Precipitation
   - pH 7.2
   - Lime
   - Zn Chloride
   - Fe Chloride
10. Co Dissolution
    - Electrolyte
11. Co Electro-winning
    - Lime
    - Fe Removal
    - Cu Precipitation
    - KO2ing
    - KO2
12. Co Spent Electrolyte
13. Electrolyte
14. Zn Spent Electrolyte
15. Cu Spent Electrolyte
16. Lime
from the quench tank at 75 - 80°C overflows into four leach tanks for further leaching of soluble copper and cobalt phases in the calcine. The final pulp pH is controlled at between 1 and 2, a range in which iron oxides and other gangue materials are hardly leached. Pulp from the leach cascade is pumped to a thickener for solid and liquid separation. A flocculant superfloc (Nåmå) is added to aid settling of solids. The overflow from the thickener goes to a solution storage tank then to the copper tankhouse for electrowinning. The copper advance electrolyte has the following composition:

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<tr>
<td>Fe</td>
<td>2 - 3 gpl</td>
</tr>
<tr>
<td>Cu</td>
<td>35 - 45 gpl</td>
</tr>
<tr>
<td>Co</td>
<td>15 - 20 gpl</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>30 - 40 gpl</td>
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The thickener underflow goes for filtration and the filtrate obtained is recycled to the thickener while the filter cake is disposed after neutralisation.

The copper tankhouse consists of an electrowinning and an electrostripping section. The electrowinning section produces physically adherent cathodes while the electrostripping produces spongy non adherent cathodes. Electrostripping further reduces as much as possible the amount of copper in the electrolyte. The copper spent electrolyte has 0.5-1.5 gpl copper and 8 - 12 gpl cobalt. The electrochemical reactions involved are as follows:

**Cathode reaction**

\[ \text{Cu}^{2+} + 2e^- = \text{Cu} \]

The acid concentration in the electrolyte increases due to the reaction:
2H⁺ + SO₄²⁻ = H₂SO₄.

Spent liquor stripped from electrostripping is pumped to a ferric cascade of five tanks. To the tanks, lime is added to raise the pH to 4.6 - 5.4 and the concentration of iron is reduced due to the fact that at this pH, iron precipitates as ferric hydroxide and is separated from the solution in a thickener. Aeration is also done to oxidise ferrous ions to ferric hydroxide.

By this precipitation, the concentration of iron is reduced to <0.05 ppm. The thickener overflow with 0.5 ppm copper and 7 - 10 gpl Co is pumped to the clean-up cascade. In the clean-up cascade more lime is added to obtain a pH of 7.0 - 7.2 and at this pH impurities such as Zn and Cd are precipitated as hydroxides. The material from the clean-up cascade then gravitates into a thickener to separate precipitated solids from the liquids. When the thickener underflow is at a density above 1.16 it is pumped to the ferric cascade while when the density is less than 1.16, the overflow is recycled to the thickener. After the clean-up cascade the thickener overflow has a cobalt concentration of 4 - 8 gpl and is pumped to the cobalt hydroxide precipitation cascade. In the cobalt hydroxide cascade, lime is again added to attain a terminal pH of 8.3 at which almost all the cobalt precipitates. This pulp then gravitates to a thickener for separation of cobalt hydroxide from the liquid. The thickener overflow is essentially water which is pumped to an effluent disposal tank. This stage is the main dewatering point. The thickener underflow at a density of 1.08 - 1.14 goes for filtration. The filtrate is recycled to the first tank of the cobalt hydroxide cascade. The cobalt hydroxide filter cake is repulped in cobalt spent electrolyte. Sulphuric acid is added to the spent electrolyte in order to attain a pH of 6.2 - 6.4. The resultant pulp gravitates to a thickener to which a flocculant is added to ensure solids settle and an overflow of
sufficient clarity is obtained. The overflow has the following typical compositions:

- **Co**: 35 gpl
- **Cu**: <0.5 gpl
- **Ni**: 0.6 - 0.8 gpl
- **Fe**: <1 gpl
- **Zn**: 0.5 gpl
- **S**: 0.4 gpl

After solution clarification, this liquid is fed to the cobalt tankhouse electrolyte. The electrolyte has to be purified to an acceptable level by removing impurities prior to electrowinning. For the removal of suspended solids, the electrolyte is passed through pre-coat filters. The pre-coat filters are fitted with 20 filter leaves while the pre-coat material is diatomaceous earth. Following the removal of suspended solids, the electrolytes then passes through carbon columns. The carbon is held in stainless steel cylindrical vessels of 1.83m diameter and 3.04m height. Each column is equipped with electrolyte flow rate indicator, upper and lower stage pressure gauges and eight carbon trap discharge Johnson screens. The carbon columns are loaded with 15 -20 tonnes of activated carbon granules which are used to reduce the amount of sulphides in the electrolyte to an acceptable level. The last electrolyte purification step utilizes two ion exchange columns for nickel removal. These columns are loaded with a resin (DOW XFS 4195) whose bed volume totals about 6.0 m³ which reduces the amount of nickel from the electrolyte to less than 0.34 gpl. The liquor (cobalt advance electrolyte) is then passed through heat exchangers to raise its temperature from 40 -45 to 55 - 60°C prior to electrowinning. The cobalt electrowinning tankhouse comprises eight cells. Each cell has twelve stainless steel cathodes and thirteen antimonial lead anodes. Electrowinning is carried out by passing a current between electrodes to achieve a current density of about 260
Am²⁺. Each cathode has a wetted area of 1.55 m². Cobalt in the electrolyte is deposited onto the cathode by means of the following chemical reactions.

**At the cathode**

\[ \text{Co}^{2+} + 2e^- = \text{Co} \]

The acid concentration in the electrolyte increases due to the reaction

\[ 2\text{H}^+ + \text{SO}_4^{2-} = \text{H}_2\text{SO}_4 \]

The cathodes are pulled out after four days and the cobalt metal manually stripped from them. After stripping, the cobalt is crushed and degassed. Degassing done at 800 ± 50°C, removes hydrogen. The metal is then polished, weighed, packed and marketed.
CHAPTER TWO

REGENERATION OF ACTIVATED CARBON USING A THERMAL METHOD

2.1 THEORETICAL

The thermal method is one way of restoring the activity of spent (exhausted) carbon. In this method, spent carbon is heated in an inert atmosphere since in an oxidising atmosphere carbon would burn and be lost. The following parameters have an important influence on the removal of adsorbates by the thermal method: temperature, furnace atmosphere and residence time of spent carbon in the furnace.

As mentioned earlier it was ensured that the furnace atmosphere was inert and this was unchanged throughout the experiments. The influence of temperature on thermal regeneration was investigated within the temperature range 600 - 900 degrees celcius. At temperatures above 900 degrees celcius even short residence times of the carbon in the furnace are likely to lead to excessive losses of activated carbon due to damage that would occur to the structure of the activated carbon [4]. At temperatures below 600 degrees celcius, very long residence times may be needed for adequate regeneration of carbon due to poor kinetics. The other experimental variable, residence time of the carbon in the furnace was investigated in the interval of 15 minutes to 4 hours.

2.2 EXPERIMENTAL

2.2.1 Materials

A bulk sample of spent granular activated carbon with a
specific surface area of 1050 ± 50 m²/g and particle size of 850 - 1000 microns 95% retain was used in the experiments. Heated copper fillings were used to oxidise any oxygen which might have been present with the nitrogen thus avoiding the incidence of carbon combustion.

2.2.2 Apparatus

The thermal regeneration experiments were conducted in an electrically heated tube furnace 50 cm long and with an internal diameter of about 3 cm. The refractory working tube placed inside the tube furnace was of 3 cm diameter and about 55 cm long. Nitrogen gas was used to create an inert atmosphere in the furnace. Also used was a silica ceramic sample holder. The apparatus used was set up as shown in Fig 2.

2.2.3 Procedure

The furnace was heated to the required temperature then nitrogen gas was introduced from one end. Copper fillings were placed at the end connected to the gas cylinder. After about 5 minutes, 5 g of carbon was put on a sample holder and pushed to the centre of the furnace. The experiments were done at different isothermal temperatures (600 - 900 degrees celcius) and for different durations (15 mins - 4 hrs).

At the end of each experiment, the furnace was switched off and the carbon particles allowed to cool within the furnace. When the carbon was cool it was removed from the furnace and analysed for regeneration efficiency.

2.2.4 Analysis
FIGURE 2: EXPERIMENTAL SET UP FOR THE THERMAL REGENERATION METHOD
The regenerated carbon particles as obtained above were analysed for regeneration efficiency by using eosin dye solution. 5 g of the regenerated carbon sample was added to 200 ml of 20 ppm eosin dye solution and the mixture agitated for one hour. The colour was analysed using a uv/visible spectrophotometer. 5 g of fresh carbon sample was similarly treated to facilitate determination of the degree of regeneration. The readings from the spectrophotometer were taken and regeneration efficiency was calculated as shown below.

\[
\text{Absorbance (fresh carbon) - absorbance (spent carbon)} \times 100
\]

\[
\text{absorbance (fresh carbon)}
\]

= efficiency

2.3 RESULTS AND DISCUSSION

2.3.1 Effect of residence time on thermal regeneration

Figure 3 shows the effect of different residence times on regeneration of activated carbon when the temperature was kept constant at 700 degrees celcius. The data on which this graph is based is contained in Table 1 which is given in the appendix.
FIGURE 3: REGENERATION EFFICIENCY OF ACTIVATED CARBON AT VARIOUS RESIDENCE TIMES.

It can be seen from Fig 3 that the regeneration efficiency at 15 minutes is as low as 58%. With increase in residence time, the regeneration efficiency increased and reached a maximum of 93% at the residence time of 120 minutes. Further increase in residence time did not yield any increase in the regeneration efficiency. This may be explained by the fact that total regeneration is not possible.
2.3.2 Effect of temperature on thermal regeneration

After residence time was optimised at 120 minutes, it was used to investigate the effect of temperature on thermal regeneration of spent activated carbon. The effect of temperature on regeneration as measured by the regeneration efficiency was established and the results on which the plot is based is contained in Table 2 given in the appendix.

![Graph showing regeneration efficiency vs temperature](image)

**FIGURE 4: REGENERATION EFFICIENCY OF ACTIVATED CARBON REGENERATED AT DIFFERENT TEMPERATURES**

It can be seen from Fig. 4 that at a temperature of 600
degrees celcius regeneration is negligible being at a low efficiency of 30%. However, with increase in temperature and for a constant residence time of 120 minutes, the regeneration efficiency also increased. At the temperature of 700 degrees celcius the regeneration efficiency was 93% and with further increase in temperature, there was a slight decrease in regeneration efficiency. This may have been due to small increase in volume of micropores and macropores owing to the removal of small amounts of adsorbed substances thus creating a loss of active sites.
CHAPTER THREE

REGENERATION OF ACTIVATED CARBON USING CHEMICAL METHODS

3.1 THEORETICAL

Chemical methods of spent carbon regeneration utilize acids or alkalis to achieve desorption of adsorbates on carbon. In this method sulphide anions are desorbed by reacting with $H^+$ cations as shown below:

$$2H^+(aq) + S^{2-} (aq) = H_2S (aq)$$

The following parameters have an influence on the chemical regeneration of activated carbon:

(i) Contact time (time of contact between the carbon particles and the regenerant). Time was investigated between the range 2 minutes and 4 hours.

(ii) The solid - liquid ratio (the volume of the regenerant that has to regenerate a certain mass of carbon particles). In this case mass of the carbon was kept constant while the volume of the regenerant was varied.

(iii) The regenerant type (only hydrochloric acid and a mixture
sulphuric acid plus potassium dichromate were investigated).

(iv) Concentration of the regenerant

(v) Agitation. This however was not investigated because it would lead to fragmentation of the carbon.

All parameters studied were investigated at ambient temperature and their effect on the extent of regeneration of spent carbon determined.

3.2 **EXPERIMENTAL**

3.2.1 *Materials*

The source of spent carbon used in the chemical regeneration experiment was as explained in the previous chapter. Two types of regenerants were used in separate experiments. These regenerants are hydrochloric acid and a mixture of sulphuric acid and potassium dichromate.

3.2.2 *Apparatus*

The apparatus used was essentially a 500 ml burette, held vertically in a stand. Into the burette a bed of activated carbon to be regenerated was placed and this
bed was supported by cotton wool. The regenerant was then passed through the bed of carbon. A 1000 ml beaker was used to collect the regenerant after it passed through the bed of activated carbon. Fig 5 shows the experimental assembly which was used.

3.2.3 Procedure

A 30 g sample of carbon particles was first washed with water to remove the cobalt advance electrolyte physically held on the particles. The washed carbon was then put into a burette to form a bed supported by cotton wool. A known volume of the regenerant was made to percolate through the bed of carbon thus causing regeneration to occur. The regenerated sample was then analysed for regeneration efficiency.

3.2.4 Analysis

The determination of regeneration efficiency was done as explained in the previous chapter.

3.3 RESULTS AND DISCUSSIONS

3.3.1 Effect of contact time on chemical regeneration

19.
FIGURE 5: EXPERIMENTAL SET UP FOR THE CHEMICAL REGENERATION METHOD.
Fig. 6 and 7 shows the extent of carbon regeneration obtained when different contact times between carbon and regenerant were used. For the hydrochloric acid regenerant, the variables kept constant were: regenerant concentration (40 gpl) and the volume of regenerant used (400 ml). For sulphuric acid and potassium dichromate regenerant, the variables kept constant were: regenerant concentration (100 gpl H₂SO₄ and 2 gpl K₂Cr₂O₇) and volume of regenerant used (400 ml). Data on which these figures are based is shown Tables 3 and 4 given in the appendix.

**FIGURE 6:** REGENERATION EFFICIENCY OF ACTIVATED CARBON REGENERATED AT VARIOUS CONTACT TIMES (40 gpl HCL REGENERANT, VOLUME OF REGENERANT, 400 ml; MASS OF CARBON, 30 g)
FIGURE 7: REGENERATION EFFICIENCY OF ACTIVATED CARBON

REGENERATED AT VARIOUS CONTACT TIMES (100 gpl H₂SO₄, -2 gpl K₂Cr₃O₇, REGENERANT; VOLUME OF REGENERANT, 400 ml; MASS OF CARBON, 30 g)

As can be seen from the figures, the regeneration efficiency, with both chemical regenerant increased with increase in contact time. Considering the HCl regenerant, after about 90 min of contact with the carbon, the regeneration efficiency reached a maximum and there was no further increase in regeneration efficiency. The maximum regeneration efficiency of 93% reached could not be exceeded due to the fact that as a rule, as
mentioned earlier, total regeneration can not be fully achieved.

In the case of the H$_2$SO$_4$ and K$_2$Cr$_2$O$_7$ regenerant, the optimal contact time was 50 minutes at which the regeneration efficiency was 90%. Even after 90 minutes of contact, the regeneration efficiencies could not be increased further.

Effect of the volume of regenerant used.

The optimised contact times were 90 minutes and 50 minutes for HCl regenerant and H$_2$SO$_4$ - K$_2$Cr$_2$O$_7$ regenerant respectively. These optimised values were kept constant in addition to the concentration of both acid regenerants which were at 40 gpl for HCL and 100 gpl - 2 gpl for H$_2$SO$_4$ - K$_2$Cr$_2$O$_7$. The volumes of regenerant used in both cases were investigated and the results are summerised in Figs. 8 and 9. The data used for the plot is given in Tables 5 and 6 given in the appendix.
FIGURE 8: REGENERATION EFFICIENCY OF ACTIVATED CARBON
REGENERATED WITH DIFFERENT VOLUMES OF 40 gpl HCL REGENERANT
In experiments with both types of regenerants, the increase in volume of regenerants used yielded an increase in regeneration efficiencies to 90% and 93% for H₂SO₄ - K₂Cr₂O₇ and HCl respectively. It was noted that the volume of the HCl regenerant used to give the optimal result is more than twice the volume of H₂SO₄ - K₂Cr₂O₇ regenerant.

3.3.3 Effect of the Concentration of regenerants
Finally after optimising the contact time and the volume of regenerant \((270 \text{ ml and } 130 \text{ ml for HCl and } H_2SO_4 - K_2Cr_2O_7 \text{ respectively})\) required and keeping them constant, the concentration of regenerant was investigated. Figs. 10 and 11 show a plot of the effect of regenerant concentration on the regeneration of spent activated carbon. The data used to plot these Figures is in Tables 7 and 8 of the appendix.

**Figure 10:** Regeneration Efficiency of Activated Carbon With Different HCl Regenerant Concentrations
FIGURE 11: REGENERATION EFFICIENCY OF ACTIVATED CARBON
REGENERATED WITH DIFFERENT H$_2$SO$_4$-K$_2$Cr$_2$O$_7$ REGENERANT
CONCENTRATION.

It can be seen from the graphs that at dilute regenerant concentration, the regeneration efficiencies are very low. As the concentrations increased the regeneration efficiencies also increased. For HCL regenerant at 40 gpl concentration the regeneration efficiency was 93% and remained the same at higher regenerant concentration. In the case of the H$_2$SO$_4$ - K$_2$Cr$_2$O$_7$ regenerant at 100 gpl H$_2$SO$_4$ and 2 gpl K$_2$Cr$_2$O$_7$ concentration the regeneration efficiency obtained was 90% and did not increase further.
CHAPTER FOUR.

COST ANALYSIS.

4.1 INTRODUCTION

Comparison of the two regeneration methods was done considering the regeneration efficiencies obtained in chapter 2 and 3. These were 90% and 93% for chemical regeneration using H₂SO₄ plus K₂Cr₂O₇ and HCL respectively and 93% for thermal regeneration. Recommendation of the suitable regenerant could not be made because the regeneration efficiencies were nearly the same for all methods.

Choice of a suitable method therefore had to depend on a cost analysis. In the cost analysis which follows the costs which will be considered are the regenerant cost for chemical regeneration and energy cost for thermal regeneration. Capital cost as well as labour for a chemical regeneration plant have not been considered as the same plant available presently could be utilized with the same manpower.

Since capital and labour have not been taken into account in the chemical regeneration cost analysis, the thermal method has not taken these into account either.
4.1.1 Cost of regenerating spent activated carbon using chemical methods

(i) Hydrochloric acid regenerant

Mass of spent activated carbon used in laboratory experiments = 30 g
Optimal regenerant concentration = 40 gpl.
Optimal volume of regenerant = 270 ml

= 270 \times 10^{-3} \text{l}

Mass of HCL used to regenerate 30 g of carbon

= 270 \times 10^{-3} \text{l} \times 40 \text{ gpl}

= 1.08 \times 10^{-5} \text{t}

To obtain the regenerant cost, the optimized regenerant requirement has been scaled up to yield the amount of regenerant which would be needed for three 20 tonne columns. 20 t of carbon can be regenerated by:

\[
(20 \times 10^6 \text{g} \times 1.08 \times 10^{-5} \text{t})/30 \text{ g} = 7.2 \text{ t HCL.}
\]

Considering that the density of HCL = 1.15 g/cm\(^3\).

Volume of HCL

= 7.2 /1.15

= 6260 \text{ l.}
Store price for 32% HCL = K279.49 per litre.[5]  

Cost of HCL for regenerating  

20 t of carbon = 279.49 * 6260  

= K1.75 m.

Typically a total of about 5 t of fresh carbon is used to top up the three columns each month. This is done because during adsorption of impurities by carbon from cobalt advance electrolyte the bed of carbon formed in the column is lost due to attrition. Therefore, 60 t of activated carbon loaded at the beginning of the operation and 5 t used to top up the three columns for twelve months (60 t) gives 120 t of spent activated carbon to be treated.

Cost of regenerating 120 t of spent activated carbon becomes:

\[
\frac{1.75 \times 120}{20} = K10.50m
\]

(ii) Sulphuric acid plus potassium dichromate.

Mass of spent of spent activated carbon used in laboratory experiments = 30 g

Optimal regenerant concentration = 100 gpl H₂SO₄. and 2 gpl K₂Cr₂O₇.

Optimal volume of regenerant = 130 ml

\[= 130 \times 10^{-3} \text{L} \]
Mass of $\text{H}_2\text{SO}_4$. used to regenerate 30 g of carbon

$$= 130 \times 10^{-3} \times 100 \text{ gpl}$$

$$= 1.3 \times 10^{-5} \text{ t.}$$

Mass of $\text{K}_2\text{Cr}_2\text{O}_7$. added to 130 ml acid (100 gpl)

$$\frac{2 \times 130 \times 10^{-3}}{100} = 0.0026 \text{ g.}$$

Store price of 98% $\text{H}_2\text{SO}_4.$ = $\text{K}68000.00$ per t [6].

Store price of potassium dichromate = $\text{K}10500.00$ per kg [7]

Again the optimized requirement scaled up,

20 t of carbon can be regenerated by:

$$\frac{20 \times 10^6 \times 1.3 \times 10^{-5}}{30} = 8.7 \text{ t } \text{H}_2\text{SO}_4.$$ 

Cost for sulphuric acid for regenerating 20 t of active carbon

$$68000 \times 8.7 = \text{K}589333.33$$

Cost of potassium dichromate for regenerating 20 t of carbon

$$6.69 \times 10500 = \text{K}70245.00$$

Total cost of regenerant used

$$= \text{K}589333.33 + 70245.00$$

= $\text{K}659578.33$

Cost of potassium dichromate and sulphuric acid for regenerating 120 t of carbon

$$= \frac{(659578.33 \times 120)}{20}$$

= $\text{K}3.96m$
4.1.2 Cost of regenerating spent activated carbon using thermal method

Thermal regeneration involves the use of rotary kilns, fluidized bed furnaces, multiple hearth furnaces, electric furnaces and tunnel kilns. In this case an electric furnace is considered as electricity is a relatively cheap source of energy in Zambia. In the analysis that follows it is assumed that about 20% of the total energy supplied to the furnace is lost during operation. This figure is typical of heat losses in such furnaces.

The cost is then calculated as follows:

Specific heat capacity \((c_p)\) of activated carbon

\[
c_p = 2.18 + 3.18 \times 10^3T - 1.48 \times 10^{-5}T^2. \tag{8}
\]

\[
dH = c_p dT
\]

\[
H = \int c_p dT
\]

Temperature optimized \(= \) 700 C (973K)

\[
H = \int_{293}^{973} (2.18 + 3.16 \times 10^3T - 1.48 \times 10^{-5}T^2) dT
\]

\[
= (2.18T + 3.16 \times 10^3T)/2 - (1.48 \times 10^{-5}T)/-1
\]

\[
H = 1.36 \times 10^9 \text{cal/mol}
\]

Conversion 1: \(1 \text{ cal} = 4.185 \text{ J}\)

\[
H = 1.36 \times 10^9 \times 4.18
\]

\[
= 5.67 \times 10^9 \text{J/mol}
\]

32
Considering that the heat loss is about 20% of the total energy to be supplied to the furnace [9].

\[ = \frac{100}{80} \times 1575 \]
\[ = 1968.75 \text{ Kwh} \]

Electrical cost \( = \text{ K1483.00 per Kwh} \) [10]

Cost for regenerating 120 t of spent activated carbon

\[ 1968.75 \times 1483 \]
\[ = \text{ K2.29m} \]
CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

Of the two methods investigated, chemical regeneration and thermal regeneration, the thermal method has been proposed for the removal of sulphide anions from spent activated carbon.

Experimental work has shown that at 700° C a regeneration efficiency of 93% can be obtained and the energy cost for doing this has been estimated as K2.92 m per 120 t of spent carbon. This method has proved to be technically feasible with lower operating cost. However, a capital cost estimation needs to be done and if this yields an acceptable cost a thermal regeneration plant could be constructed.

The chemical regeneration method has been found less competitive on the grounds of high regenerant cost. Although the regeneration efficiencies for the two regenerants were almost the same, the cost of the regenerants required is different. This was because sulphuric acid, which is locally produced, is cheaper than hydrochloric acid, an imported reagent.
REFERENCES


5. ZCCM, Nkana Division, Cobalt Plant accounts department.

6. Ibid.

7. Ibid.


10. ZCCM Nkana Division, Cobalt Plant accounts department.
APPENDICES

1. ZCCM Cobalt metal specifications

2. Tables
<table>
<thead>
<tr>
<th>Efficiency (%)</th>
<th>Residence Time (minutes)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>93</td>
<td>240</td>
<td>700</td>
</tr>
<tr>
<td>93</td>
<td>180</td>
<td>700</td>
</tr>
<tr>
<td>93</td>
<td>120</td>
<td>700</td>
</tr>
<tr>
<td>92</td>
<td>105</td>
<td>700</td>
</tr>
<tr>
<td>96</td>
<td>90</td>
<td>700</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
<td>700</td>
</tr>
<tr>
<td>65</td>
<td>30</td>
<td>700</td>
</tr>
<tr>
<td>58</td>
<td>15</td>
<td>700</td>
</tr>
</tbody>
</table>

**TABLE 1:** Amount of Activity of Carbon Resorbed at Various Residence Times When Temperature was Kept Constant.

39
<table>
<thead>
<tr>
<th>% Efficency</th>
<th>Regeneration Time (minutes)</th>
<th>Optimal Residence Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>120</td>
<td>600</td>
</tr>
<tr>
<td>92</td>
<td>120</td>
<td>00</td>
</tr>
<tr>
<td>93</td>
<td>120</td>
<td>00</td>
</tr>
<tr>
<td>93</td>
<td>120</td>
<td>00</td>
</tr>
<tr>
<td>92</td>
<td>120</td>
<td>00</td>
</tr>
<tr>
<td>90</td>
<td>120</td>
<td>00</td>
</tr>
<tr>
<td>70</td>
<td>120</td>
<td>00</td>
</tr>
<tr>
<td>30</td>
<td>120</td>
<td>00</td>
</tr>
</tbody>
</table>

At various temperatures when residence time was kept constant.

Table 2. Amount of activity of carbon restored.
<table>
<thead>
<tr>
<th>Regen (g)</th>
<th>2</th>
<th>30 g in 400 ml</th>
<th>40 g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>Regeneration Ratio</td>
<td>Contact Time 30 g to 400 ml</td>
<td>Solid - Liquid Concentration</td>
</tr>
<tr>
<td>---------------</td>
<td>-------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>65</td>
<td>C</td>
<td>100 g/ml - 2 g/ml</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>C</td>
<td>100 g/ml - 2 g/ml</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>C</td>
<td>100 g/ml - 2 g/ml</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>C</td>
<td>100 g/ml - 2 g/ml</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>100 g/ml - 2 g/ml</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: The efficiency of carbon restored at various contact times between carbon and volume of regenerant were kept constant and sulfuric acid - potassium dichromate regenerant when concentration.

AND VOLUME OF REGENERANT WERE KEPT CONSTANT
<table>
<thead>
<tr>
<th>REGENERATION</th>
<th>OPTIMAL CONTRACT VOLUME</th>
<th>VOLATILE CONCENTRATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 g/d</td>
<td>200 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>26</td>
<td>250 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>240 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>220 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>210 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>200 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>190 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>180 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>170 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>160 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>150 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>140 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>130 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>120 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>110 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>100 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>90 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>80 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>70 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>60 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>50 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>40 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>30 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>20 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>10 m³</td>
<td>40 g/d</td>
</tr>
<tr>
<td>63</td>
<td>0 m³</td>
<td>40 g/d</td>
</tr>
</tbody>
</table>

Optimal contract time and concentration of regenerant were kept constant.

Table 5. The efficiency of carbon restored using different volumes of hot regenerant when
<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Regeneration</th>
<th>Volume</th>
<th>Constant Time and Concentration of Regenerant were Kept</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>50</td>
<td>600 ml</td>
<td>100 gpt-2 gpt</td>
</tr>
<tr>
<td>06</td>
<td>50</td>
<td>400 ml</td>
<td>100 gpt-2 gpt</td>
</tr>
<tr>
<td>06</td>
<td>50</td>
<td>200 ml</td>
<td>100 gpt-2 gpt</td>
</tr>
<tr>
<td>06</td>
<td>50</td>
<td>120 ml</td>
<td>100 gpt-2 gpt</td>
</tr>
<tr>
<td>06</td>
<td>50</td>
<td>100 ml</td>
<td>100 gpt-2 gpt</td>
</tr>
<tr>
<td>06</td>
<td>50</td>
<td>90 ml</td>
<td>100 gpt-2 gpt</td>
</tr>
<tr>
<td>69.6</td>
<td>50</td>
<td>90 ml</td>
<td>100 gpt-2 gpt</td>
</tr>
<tr>
<td>68</td>
<td>50</td>
<td>90 ml</td>
<td>100 gpt-2 gpt</td>
</tr>
<tr>
<td>(Efficiency)(%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 6. THE EFFICIENCY OF CARBON RESTORED USING DIFFERENT VOLUMES OF SUBPHORIC ACID-POTASSIUM DICHROMATE REGENERANT WHEN OPTIMAL
<table>
<thead>
<tr>
<th>REGENERANT</th>
<th>OPTIMAL VOLUME</th>
<th>OPTIMAL CONTACT</th>
<th>CONCENTRATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>REN 1</td>
<td>270 gpt</td>
<td>60</td>
<td>100 gpt</td>
</tr>
<tr>
<td>REN 2</td>
<td>270 gpt</td>
<td>60</td>
<td>50 gpt</td>
</tr>
<tr>
<td>REN 3</td>
<td>270 gpt</td>
<td>60</td>
<td>45 gpt</td>
</tr>
<tr>
<td>REN 4</td>
<td>270 gpt</td>
<td>60</td>
<td>40 gpt</td>
</tr>
<tr>
<td>REN 5</td>
<td>270 gpt</td>
<td>60</td>
<td>30 gpt</td>
</tr>
<tr>
<td>REN 6</td>
<td>270 gpt</td>
<td>60</td>
<td>20 gpt</td>
</tr>
<tr>
<td>REN 7</td>
<td>270 gpt</td>
<td>60</td>
<td>10 gpt</td>
</tr>
</tbody>
</table>

EFFICIENCY (%) | TIME (Minutes) |

Table 7. The efficiency of carbon restored using various NO. REGENERANT.
<table>
<thead>
<tr>
<th>% Efﬁciency</th>
<th>Time (Minutes)</th>
<th>Optimal Volume</th>
<th>Optimal Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>06</td>
<td>06</td>
<td>130</td>
<td>100 gp 1-2 gpt</td>
</tr>
<tr>
<td>06</td>
<td>06</td>
<td>130</td>
<td>100 gp 1-2 gpt</td>
</tr>
<tr>
<td>06</td>
<td>06</td>
<td>130</td>
<td>100 gp 1-2 gpt</td>
</tr>
<tr>
<td>06</td>
<td>06</td>
<td>130</td>
<td>100 gp 1-2 gpt</td>
</tr>
<tr>
<td>88</td>
<td>06</td>
<td>130</td>
<td>100 gp 1-2 gpt</td>
</tr>
<tr>
<td>88</td>
<td>06</td>
<td>130</td>
<td>100 gp 1-2 gpt</td>
</tr>
<tr>
<td>88</td>
<td>06</td>
<td>130</td>
<td>100 gp 1-2 gpt</td>
</tr>
<tr>
<td>88</td>
<td>06</td>
<td>130</td>
<td>100 gp 1-2 gpt</td>
</tr>
<tr>
<td>74</td>
<td>06</td>
<td>130</td>
<td>100 gp 1-2 gpt</td>
</tr>
<tr>
<td>60</td>
<td>06</td>
<td>130</td>
<td>100 gp 1-2 gpt</td>
</tr>
</tbody>
</table>

Table 8: The Efﬁciency of Carbon Resin and Using Various Sulfuric Acid

Volume of resin was kept constant.

Potassium dichromate concentration when Optimal Concentration and Optimal Volume are determined.