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REGENERATION OF ACTIVATED CARBON USED FOR RECOVERY OF GOLD

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Abstract: The process of treating granular activated carbon for return to service in the recovery of gold in Carbon in Pulp and Carbon in Leach circuits has been investigated. Carbons from four U.S.A. mines, one Canadian mine and one South African mine were characterized before and after regeneration. The use of thermal gravimetric analyses demonstrated the presence of inorganic compounds on the surface of the carbon. Thermal regeneration was investigated using factorial analysis to determine the effect or interaction of furnace temperature, retention time and the use of supplemental steam. The operation of acid leaching prior to or after gold elution was investigated. The effect of water quenching regenerated carbon was also studied. From the data obtained in this investigation, guidelines are given for effective regeneration operation.

Introduction

The Carbon in Pulp (CIP) and Carbon in Leach (CIL) processes for recovery of gold have become increasingly important in the gold industry. Therefore, it is also important to understand the unit processes in the CIP/CIL operations which could affect the condition of the activated carbon. Carbon pretreatment and regeneration procedures developed thus far have been derived from mine experience generally through trial and error approaches. For our investigation, regenerations using factorial analyses were performed on carbon samples to determine the effects of time, temperature and steam. The work reported here attempts to delineate factors which affect regeneration of carbon.

Experimental

Carbon Characterization

Iodine Number was obtained using Calgon Test Method 4.[1] Carbon tetrachloride, apparent density and total ash testing was done according to ASTM methods.[2]

Iodine Number (I_2 No.) is a measure of the amount of iodine adsorbed per gram of carbon and gives an indication of the available surface area of the carbon. Carbon tetrachloride (CCl_4) activity is the weight (%) of CCl_4 adsorbed on the carbon and gives an indication of the activation level of the activated carbon.

The K-Value and rate test R-Value are Calgon adaptions of Mintek and Anglo American Research Laboratories (AARL) test methods[3] and are measurements of gold capacity and rate of gold removal, respectively.

Stripping/Elution

The carbon samples from the South African CIL pilot plant were stripped by contacting them with 3% HCl at ambient conditions for one hour. This was followed by a neutralization with 1% Na_2CO_3 at ambient conditions and two bed volumes (B.V.) of distilled water (D.I.) at 120°C. Gold elution of the carbon samples was performed using a pressurized system by pumping a 2% NaCN/1% Na_2CO_3 solution through the carbon at 120°C until an alkaline pH ($\approx$ 11) was detected. The carbon was then allowed to soak for one hour maintaining a temperature of 120°C. After one hour, seven bed volumes of distilled water were pumped through the carbon bed also at 120°C.

Gold elution of the loaded carbon sample from mine D was accomplished in the lab using the following procedure based on plant operations. The carbon was acid washed with one bed volume of either 3.5% V/V HNO_3 or 3% V/V HCl. The carbon was then washed with one bed volume (B.V.) D.I. water followed by one B.V., 1% Na_2CO_3 and one B.V. D.I. water. The carbon was then drained. One B.V. of 0.5% NaCN/1% NaOH solution was applied and the carbon allowed to soak overnight at 77°C. The carbon was then heated to 120°C and 12 B.V. of hot (120°C) distilled water was pumped through the column.

Regeneration

All thermal regenerations were conducted using a two-inch externally heated rotary tube furnace. In order to simulate an expected plant condition of 50 percent moisture in the carbon prior to regeneration, 100g of oven dried material was placed in a 250 ml jar and 50g of D.I. water was added. The jar was then tightly capped and the carbon allowed to equilibrate. Additional water, when required, was added by pumping the required volume of water through a steam super heater prior to entering the rotary furnace. The pump rate was adjusted to give the additional water required over the course of the regeneration retention time. The 100g charge of wetted carbon was placed in a nichrome 60 mesh basket assembly which was then quickly introduced into the tube furnace and the end cap securely fastened. After the required time, the carbon and basket assembly was removed, then cooled in a sealed cooling chamber.

Acid Washing

Acid washing consisted of batch contacting the carbon with one B.V. of acid for one hour. The carbon was then washed sequentially with two B.V. D.I. water, one B.V. 1% Na_2CO_3, and two B.V. D.I. water.

Quenching

Lab quenching consisted of pouring the hot regenerated product immediately after furnace discharge into 1,000 ml of D.I. water contained in a 3L metal beaker. A portion of the quenched carbon was dried at 120°C in a nitrogen gas environment to eliminate any possible chemisorption of oxygen. Another portion was dried at 120°C in a lab oven with no attempt to control the environment.

Carbon Characterization

Samples of carbon before and after plant regeneration were obtained from the four U.S. mines and one Canadian operation. These samples had been in service for various periods of time. Their exact service history is not known. No regenerated samples were obtained from the South African operation. Table I is a listing of some of the parameters used to characterize the carbons.

Samples from U.S. mines labelled A&B are low activity coconut carbons and the rest of the samples can be designated as high activity coconut carbons. The low activity coconut carbons used by Mines A&B have the following characteristics. CCl_4 = 25-30; K-Value = 20-25 and R-Value of .03-.05. The activity characteristics of the carbon used by Mines C-G are CCl_4 = 60-65; K-Value = 30-35 and R-Value = .075-.085. Inspection of the gold capacity parameters of R-Value and K-Value for all carbons show that virgin activity levels were not restored by regeneration. This could lead one to conclude that thermal regeneration, as performed, at the four U.S. mines and the Canadian operation does not fully restore gold activity.

Thermal Gravimetric Analyses

Figures 1 and 2 are typical of the TGA plots obtained using a DuPont Model 1090 Thermal Analyser on spent and regenerated carbons with high ash contents (A, B & C). The plots show removal of moisture at approximately 100°C, a slow decline in weight at a steady rate to approximately 500-600°c, then an increase in weight loss rate at a temperature >600°C.

In an attempt to simulate inorganic loading on carbon, the calcium ion, which is abundant in CIP and CIL processes, was impregnated on a sample of regenerated Carbon D using $Ca(OH)_2$ (1% Wt Ca). The carbon was then exposed to CO_2. The regenerated Carbon D did not show the weight loss increase at 600-700°C. Figure 3 is the TGA plot obtained and shows an increase in weight loss rate between 600 and 700°C. From this, one may conclude that the observed change in weight loss rate at 600-700°C is due to the decomposition of carbonates. It is interesting to note that operations D and E incorporate acid wash steps before regeneration (either before or after stripping), thereby reducing carbonate content. The TGA plots for these carbons did not exhibit this weight loss change. TGA plots of carbons A, B and C after lab acid washing showed a significant decrease in this weight loss rate at 600-700°C.

Determination of Optimal Regeneration Conditions Using Carbons From South African Mine

Initially, a factorial experiment was designed to determine the effect of furnace retention time, regeneration temperature and steam addition. Prior to regeneration, the loaded carbon samples were laboratory stripped and eluted. After the HCl strip and elution with a Na_2CO_3/NaCN solution using the previously described procedure, ash was reduced slightly with minor increases in CCl_4 and Iodine Number. Adsorption rate (R) was significantly lower than virgin carbon.

The first four experiments are a half replicate of the 2^3 factorial and Experiments 5 and 6 were run to further define the most significant variable determined by the results of the half replicate. The temperature ranges and times were selected by surveying nine mining operations in the U.S., Canada and South Africa. The lower water level (0.5 lb/lb C) is approximately equivalent to water carried into the furnace by drained activated carbon. The second level was obtained by injecting an amount of steam (0.5 lb H_2O/lb carbon) equivalent to that on the feed carbon so that the total steam was 1 lb H_2O/lb carbon.

The results of experiments for F and G carbons are listed in Tables 3 and 4, respectively. All the K-Values are comparable to virgin Table 2, while R-Values vary. R-Value, which is an indication of rate, is generally considered to be a more important parameter compared to K-Value and also appears to be a better indication of regeneration.

Ash data for both carbons revealed a decrease in ash content compared to the ash content of the eluted samples. This indicates that thermal regeneration removed or decomposed ash constituents in addition to any organic material adsorbed on the carbon. Typically, thermal regeneration of spent activated carbon is conducted to remove organic adsorbates. As shown by the ash values in Tables 2 (eluted), 3 and 4, the major reduction obtained is inorganic decomposition. The ash reduction could be accounted for by the decomposition of carbonates, as shown by the TGA analyses in addition to cyanides and cyanates.

An approach to examining the true condition of the carbons is to discount ash from virgin, eluted and regenerated carbons. This was done in calculating an ash free apparent density. The values are listed in Tables 3 and 4 under A.D. in brackets. F carbons were restored to near virgin rate values for most of the experiments. In Experiment 1, supplemental steam at 650°C returned both rate and ash free A.D. to virgin levels in nominal retention time. Doubling the time (Experiment 3) without added steam shows no further benefit. Without steam at 650°C (Experiment 5), recovery of rate and CCl_4 was not as complete. Experiments 4 and 6 indicate that activation was taking place as activity was increased, but at the expense of attacking the base carbon. This is confirmed by the lower than virgin ash free apparent densities. These observations lead to the conclusion that more control over regeneration is possible at lower temperatures with additional steam. Regeneration of the G samples (Table 4) shows a somewhat similar pattern.

At the present time, the high R-Value in Experiment 1 is unexplainable since the ash free A.D. is still above virgin (0.490 g/cc).

Complete regeneration of both carbons, as evidenced by R-Value, was achieved at 650°C in 20 minutes with 0.5g H_2O/lb C added steam. Times longer than 20 minutes were not a major factor at both temperatures without added steam. At 850°C with added steam, activation of both carbons occurred as evidenced by an increase in R-Value above virgin values and a decrease in base carbon.

Additional Regenerations

Based on the results of the factorial experiments, two conditions were selected to perform lab regenerations on samples A-E.

The results (Tables 5 to 9) indicate that all laboratory regenerated carbons had significantly higher adsorption rates when compared to plant regenerated samples.

Two carbon samples each were obtained from plants A, B and C representing the kiln feed (as received) and kiln discharge (plant reg). Since the plants do not use any acid washing in the process, a sample of kiln feed was lab acid washed with HCl to determine effects. Tables 5, 6 and 7 show that acid washing reduced the ash slightly, increased the CCl_4 value, but gave no improvement in rate.

The carbons from plants A and B appear to require higher temperature and longer residence time to achieve the expected values of low activity virgin coconut carbon. Unlike carbons F and G, it appears that these carbons are contaminated with organic materials since there is no significant decrease in ash accompanying the improvement in R-Value.

The data in Table 4 show that acid washing alone would restore 60% of the original gold adsorption rate to the carbon from mine C. Note that the R-Value for plant regeneration is only 40% of virgin carbon. Thermal regeneration further restores R-Value. This is probably due to organic removal.

Analyses of samples from mine D show that the carbon operation at this mine is the best of all the mines investigated.

Carbon samples of loaded, eluted and plant regenerated with and without water quenching were received from plant D. This plant includes an acid wash step prior to gold elution. Laboratory elutions were conducted to evaluate the effects, if any, of acid washing with HCl versus HNO_3. As shown in Table 8, no significant effects between HCl and HNO_3 were obtained. Both acids gave improvements in I_2 and CCl_4 values to near react values, but the gold activity parameters of K and R were approximately 50% of react values, indicating thermal regeneration is necessary to restore gold activity parameters. Inspection of the results on the plant stripped lab regenerated carbons for both condition indicate that a slight activation at the base carbon may have occurred. This is further suggested by the lower yields obtained under both conditions. Ash reduction was evident for the stripped carbon regenerated under both conditions. Both the lab quench and plant quench results indicate that water quenching reduces activity. Work is continuing to determine the relative effect of air cooling versus water quenching.

Carbon samples of eluted, acid washed and plant regenerated samples were received from Plant E. Acid washing follows elution in this operation. Lab acid washing was done on the eluted sample to compare HCl to HNO_3. The results, Table 9, indicate no discernable difference between HCl and HNO_3, but does show some benefit after thermal regeneration in R-Value due to acid washing for both the lab acid washed and plant acid washed carbon samples. It appears that the major contaminant for Carbon E is organic material since little, if any ash reduction occurs with the significant improvement in K and R-Values. It also appears that the virgin A.D. of Carbon E is somewhat higher than the other carbons as evidenced by ash free regenerated A.D. of .55-.56, compared to .50-.52 for the other high activity coconut carbons. Results of the quenching study done on acid washed carbon shows a reduction in K and R-Values for the lab regenerated samples. Note that the lab quench values are better than the plant quench values for gold capacity and rate of removal.

It is hypothesized that the long-term use of HNO_3 for acid washing to remove metal precipitates such as $CaCO_3$ from carbon used in the CIP process can result in an oxidation of the carbon particle over an extended period. Efforts were made during these studies to demonstrate this effect, but there was insufficient time for multiple cyclic exposure.

Previous experiments at Calgon Carbon have shown that carbon boiled a few minutes in a 10% HNO_3 solution contained 10% wt oxygen after drying at 150°C. The oxygen can be stripped at 450°C but only CO + CO_2 are detected in the off gases. From this, it may be concluded that repeated contact with HNO_3 without adequate rinsing will result in a loss of carbon to the extent that the physical integrity of the particle will be impaired resulting in excessive losses. Work is continuing in this area.

Conclusions

Thermal regeneration of gold recovery carbons is necessary to restore gold capacity as measured by K and R-Values.

Thermal regeneration can result in a reduction of ash constituents in addition to the removal of adsorbed organic materials.

The application of supplemental steam will allow a plant to operate their kiln at a lower temperature and shorter residence time to achieve virgin activity levels if inorganics are the main contaminant.

Acid washing will reduce inorganic ash on the carbon and can restore I_2 and CCl_4 values to near virgin carbon activity levels, but does not restore the gold activity parameters of K and R-Values to this level.

High temperature and long residence time with supplemental steam, can result in a loss of base carbon due to activation.

References

1. Calgon Test Method 4, "Determination of the Iodine Number of Activated Carbon," Calgon Corporation, Box 1346, Pittsburgh, PA 15230.

2. ASTM Method D3467-76(1983), "Carbon Tetrachloride Activity of Activated Carbon."

ASTM Method D2854-83, "Apparent Density of Activated Carbon."

ASTM Method D2866-83, "Total Ash Content of Activated Carbon."

Published in 1984 Annual Book of ASTM Standards Section 15.

3. Calgon Test Method 53 "Determination of the Gold Adsorptive Capacity (K-Value) of Activated Carbon.

Calgon Test Method, "Gold Adsorption Rate Test," August 1983.

Table 1. Carbon Characterization Before and After Plant Regeneration

	A		B		C		D		E		F	G
Plant Designation	Before	After	Before	After	Before	After	Before	After	Before	After	Before	Before
A.D.	.731	.722	.903	.756	.651	.575	.528	.532	.60	.636	-	-
Ash %	5.1	6.1	11.1	10.4	7.9	6.6	3.4	2.2	2.3	2.9	24.5	8.5
I_2 No., mg/g	745	759	598	653	964	996	1060	1065	1018	1045	902	894
CCl_4 - % Wt	20	21	2.5	18.5	31.9	54.3	55	57	50.5	55.1	48.3	41.5
R-Value	-	.0097	-	.019	-	.034	.035	.043	.029	.045	-	-
K-Value, mg/g	<15	<15	<15	<15	<15	<15	20.5	21.6	22.6	24.5	<15	<15

A, B, C & D = U.S. Mines

E = Canadian Mine

F & G = S. African Mine

A & B are low activity coconut carbons.

C, D, E, F & G are high activity coconut carbons.

Table 2. Carbon Characteristics

	F		G	
	Virgin	Eluted	Virgin	Eluted
A.D.	0.498 (0.487)*	0.539 (0.499)	0.499 (0.490)*	0.561 (0.493)
Ash	2.2	7.4	1.9	12.2
I_2 No.	1200	930	1380	918
CCl_4 No.	62.4	44.7	68.9	48.8
R-Value	0.082	0.022	0.080	0.015
K-Value, mg/g	30.8	<15	32.4	<15

*Ash Free

Table 3. Carbon F Regeneration Results

Experiment Number	Time (min.)	Temp. °C	Steam lb H_2O/lb C	Yield %-Wt	A.D. g/cc		Ash %-Wt	CCl_4 No.	Rate R	Capacity K
1	20	650	1.0	91.7	0.511	(0.489)*	4.3	57.5	0.082	34
2	20	850	0.5	90.2	0.529	(0.502)*	5.1	55.2	0.080	34
3	40	650	0.5	94.4	0.526	(0.504)*	4.1	53.1	0.077	34
4	40	850	1.0	90.7	0.521	(0.472)*	6.3	61.3	0.092	32
5	20	650	0.5	90.7	0.512	(0.487)*	4.9	52.3	0.075	32
6	20	850	1.0	81.0	0.499	(0.478)*	4.2	64.6	0.086	37

*Ash Free

Table 4. Carbon G Regeneration Results

Experiment Number	Time (min.)	Temp. °C	Steam lb H_2O/lb C	Yield %-Wt	A.D. g/cc		Ash %-Wt	CCl_4 No.	Rate R	Capacity K
1	20	650	1.0	92.4	0.524	(0.506)*	3.4	66.8	0.095	33.3
2	20	850	0.5	92.0	0.528	(0.510)*	3.5	62.2	0.076	35.1
3	40	650	0.5	90.7	0.539	(0.520)*	3.5	62.2	0.063	34.9
4	40	850	1.0	84.1	0.504	(0.468)*	7.1	71.1	0.097	32.3
5	20	650	0.5	88.6	0.536	(0.520)*	2.9	66.0	0.069	34.0
6	20	850	1.00	80.3	0.501	(0.467)*	6.7	66.2	0.079	34.0

*Ash Free

Table 5. Carbon-A Regeneration Results

	As Received	Reg. Cond. 1	Reg. Cond. 2	Lab A.W.	Lab A.W. Reg. Cond. 2	Plant Reg.
A.D.	.668 (.634)	.651 (.619)	.66 (.625)	.655	.658 (.63)	.70 (.657)
I_2 No., mg/g	745	845	796	-	803	759
CCl_4 - % Wt	20	33.6	31	28.5	31.5	21
Ash - %	5.1	4.9	5.3	-	4.2	6.1
Yield - Wt %	-	96.1	96.1	-	92.5	-
R	-	.057	.044	.02	.045	.02
K, mg/g	<15	34.5	26.7	-	27.5	<15

( ) Ash Free A.D.

Cond. 1 = 700°C - 40 Minutes - 0.5 lb H_2O/lb Carbon
Cond. 2 = 600°C - 20 Minutes - 1.0 lb H_2O/lb Carbon

Table 6. Carbon-B Regeneration Results

	As Received	Reg. Cond. 1	Reg. Cond. 2	Lab A.W.	Lab A.W. Reg. Cond. 1	Plant Reg.
A.D.	.711 (.632)	.684 (.615)	.684 (.618)	.698	.681 (.62)	.719 (.644)
I_2 No., mg/g	598	710	704	-	747	653
CCl_4 - % Wt	2.5	27.5	28.1	26.7	31	18.5
Ash - %	11.1	10.1	9.6	-	9.0	10.4
Yield - Wt %	-	95.2	92.1	-	94.5	-
R	-	.069	.04	.026	.055	.019
K, mg/g	<15	26.8	21.2	-	280	<15

( ) Ash Free A.D.

Cond. 1 = 700°C - 40 Minutes - 0.5 lb H_2O/lb Carbon
Cond. 2 = 600°C - 20 Minutes - 1.0 lb H_2O/lb Carbon

Table 7. Carbon-C Regeneration Results

	As Received	Reg. Cond. 1	Reg. Cond. 2	Lab A.W.	Lab A.W. Reg. Cond. 2	Plant Reg.
A.D.	.63	.534	.534	.544	.527	.575
	(.58)	(.49)	(.491)		(.501)	(.537)
I_2 No., mg/g	964	1139	1112	-	1150	996
CCl_4 - % Wt	31.9	60.1	58	56	60.4	54.3
Ash - %	7.9	8.3	8.0	-	5.0	6.6
Yield - Wt %	-	95.4	95.5	-	94.8	-
R	-	.083	.069	.048	.073	.034
K, mg/g	<15	27.9	21.7	-	22.8	<15

( ) Ash Free A.D.

Cond. 1 = 700°C - 40 Minutes - 0.5 lb H_2O/lb Carbon
Cond. 2 = 600°C - 20 Minutes - 1.0 lb H_2O/lb Carbon

Table 8. Carbon-D Regeneration Results

	Eluted				Loaded					Plant Reg.	
						Lab strip 3.5 HNO_3		Lab Strip 3% HCl			
	As Received	Reg. Cond. 1	Reg. Cond. 2	Reg. Cond. 1 Quench	As Received	Before	Reg. Cond. 1	Before	Reg. Cond. 1	Quench	No Quench
A.D.	.528	.515	.509	.512	.556	.534	.524	.536	.525	.532	.518
	(.51)	(.502)	(.496)	(.502)	(.537)	(.528)	(.517)	(.529)	(.518)	(.51)	(.506)
I_2 No., mg/g	1060	1245	1219	1134	1018	1180	1128	1095	1245	1065	1134
CCl_4 - % Wt	55	59.7	63.4	55.4	48.1	52.1	55.5	51.8	60.4	57	58.4
Ash - %	3.4	2.6	2.5	2.0	3.4	1.1	1.4	1.3	1.3	4.1	2.2
Yield - Wt %	-	89.4	93.1	-	-	-	95.9	-	95.1	-	-
R	.035	.104	.109	.087	.029	.047	.097	.045	.098	.043	.065
K, mg/g	20.5	28.3	34.4	29.5	21	19.1	39.5	20.7	37.7	21.6	31.3

( ) Ash Free A.D.

Cond. 1 = 700°C - 40 Minutes - 0.5 lb H_2O/lb Carbon
Cond. 2 = 600°C - 20 Minutes - 1.0 lb H_2O/lb Carbon

Table 9. Carbon-E Regeneration Results

	Eluted					Acid Washed				Plant Reg.
	As Received	Reg. Cond. 1	Reg. Cond. 2	Reg.[A] Cond. 1	Reg.[B] Cond. 1	As Received	Reg. Cond. 1	Reg. Cond. 2	Reg. Cond. 1 Quench	Quench
A.D.	.63 (.59)	.593 (.56)	.589 (.557)	.582 (.562)	.575 (.557)	.60 (.586)	.576 (.558)	.565 (.552)	.568 (.558)	.571 (.554)
I_2 No., mg/g	964	1101	1095	1128	1139	1018	1145	1117	1138	1045
CCl_4 - % Wt	49	51.5	52	53.9	54.4	50.5	54	54.9	60.5	55.1
Ash - %	6.3	5.5	5.5	3.3	3.1	2.3	3.1	2.2	1.7	2.9
Yield - Wt %	-	96.2	95.6	96.2	95.3	-	89.7	94.4	-	-
R	.022	.072	.068	.084	.085	.029	.084	.09	.078	.045
K, mg/g	<15	33.1	26.4	29.2	29	22.6	36.3	32.8	28.6	24.5

( ) Ash Free A.D.

A = Lab Acid Wash with 3% HCl
B = Lab Acid Wash with 5% HNO_3

Cond. 1 = 700°C - 40 Minutes - 0.5 lb H_2O/lb Carbon
Cond. 2 = 600°C - 20 Minutes - 1.0 lb H_2O/lb Carbon

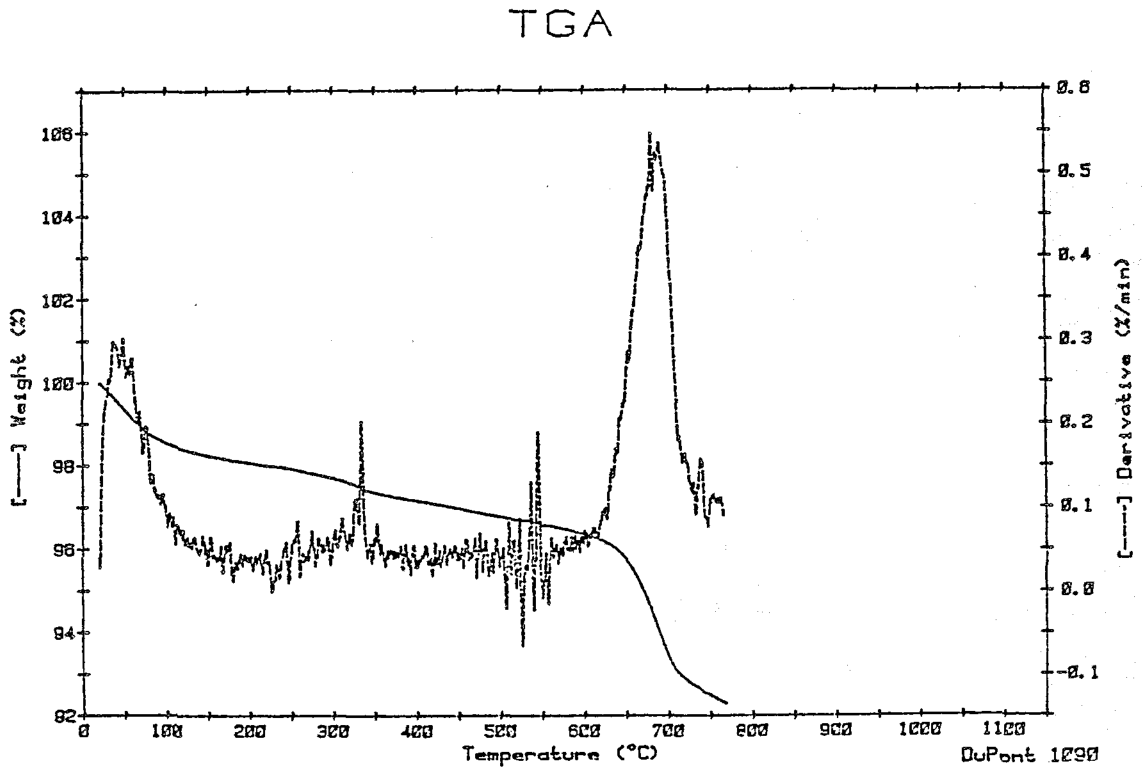

FIGURE 1 - TYPICAL TGA CURVE FOR CARBONS A, B & C BEFORE REGENERATION

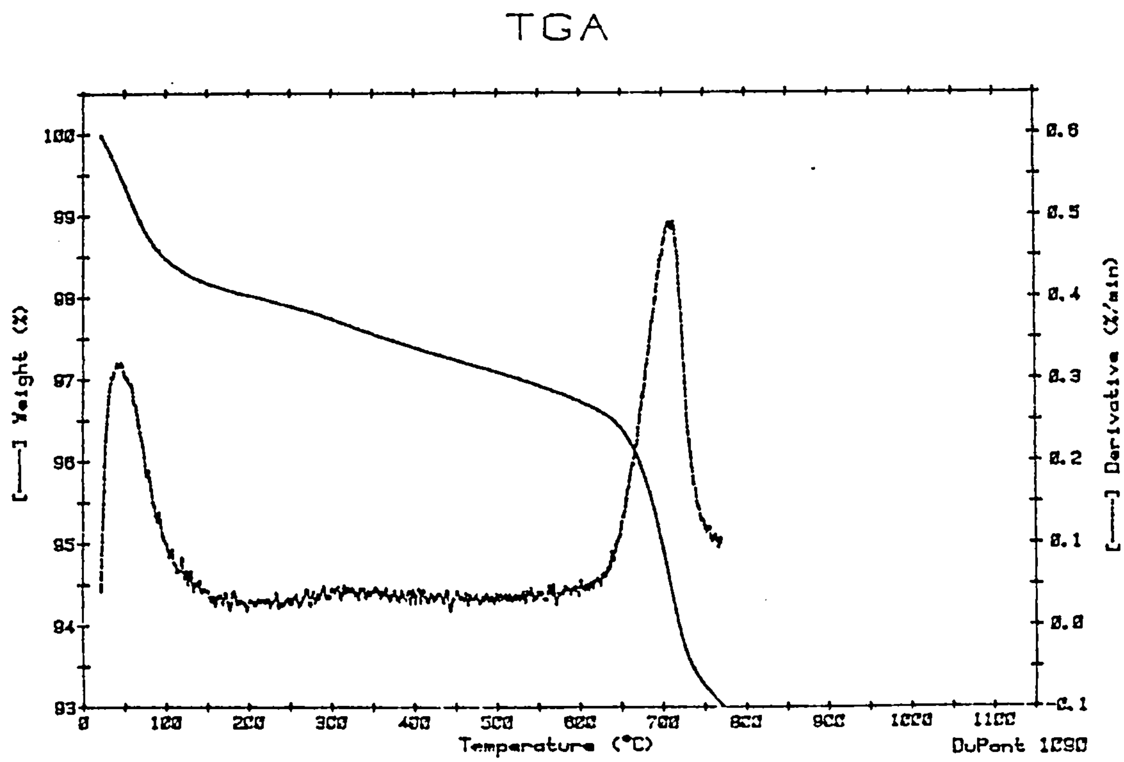

FIGURE 2 - TYPICAL TGA CURVE FOR CARBONS A, B & C AFTER REGENERATION

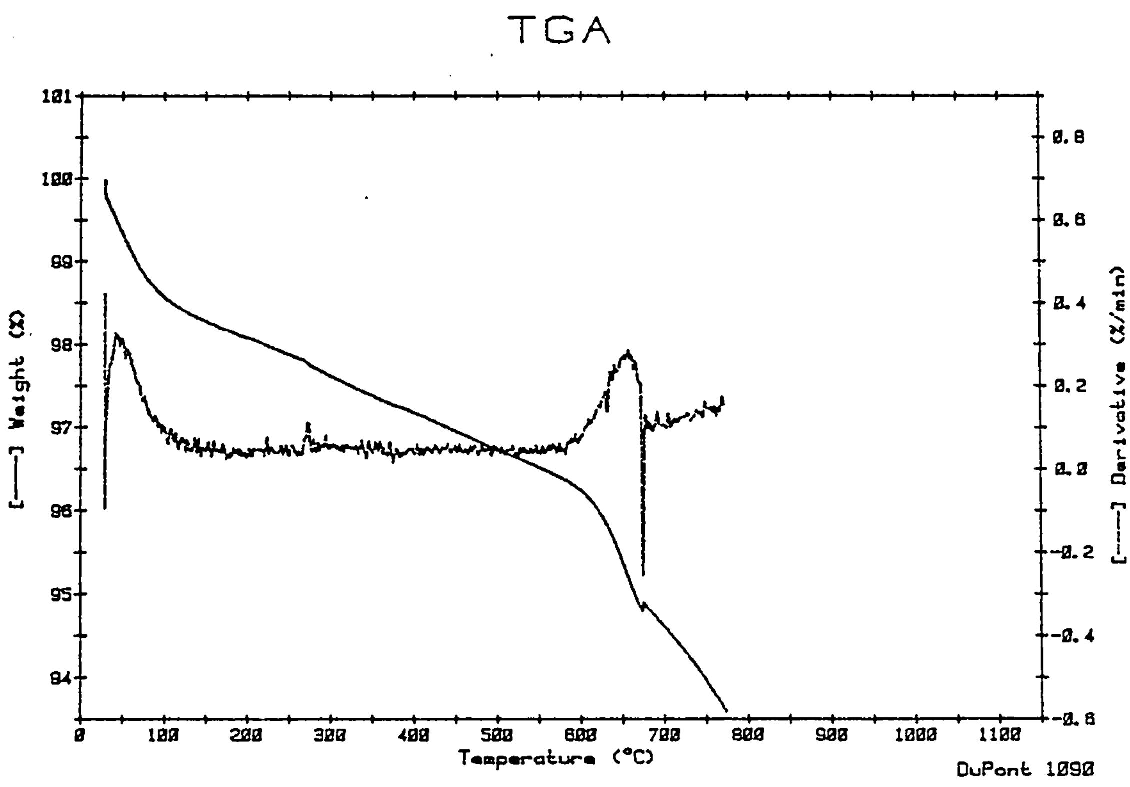

FIGURE 3 - CARBON D IMPREGNATED WITH 1% $CaCO_3$