The adsorption of dissolved gold on activated charcoal in a NIMCIX contactor

by D. I. NICOL*, B.Sc. (Chem. Eng.) (Visitor)

SYNOPSIS

An assessment is made of the possible scope for the use of activated charcoal as the solid adsorbent in an upflow fluidized-bed contactor, and a pilot-plant programme for the recovery of low concentrations of dissolved gold in this contactor is described. It was found possible to produce an effluent that contains less than 0,01 p.p.m. of dissolved gold.

SAMEVATTING

Die moontlike omvang van die gebruik van geaktiveerde houtskool as die soliede adsorbeermiddel in 'n opvloeifluïedbedkontaktor word geëvalueer en 'n proefaanlegprogram vir die herwinning van lae konsentrasies opgeloste goud in hierdie kontaktor word beskryf. Daar is gevind dat 'n uitvloeisel verkry kan word wat minder as 0,01 d.p.m. opgeloste goud bevat.

Introduction

Metallurgical interest in activated charcoal as an adsorbent for dissolved gold can be traced back to as far as 1880, when Davis patented a process for the adsorption of gold on activated charcoal in the chlorination process[1]. The subsequent history of the use of activated charcoal in this process, and later in the cyanide process, has been described by Gross and Scott[2].

In the early applications of activated charcoal on a commercial scale, the gold-laden charcoal was usually burnt to ashes and then smelted to bullion. This burning and smelting operation resulted in the total destruction of the activated charcoal, and its replacement cost, excluding the freight charges, was high — about 3 U.S. dollars per ounce of gold recovered in 1963[3].

In 1952 a laboratory and pilot-plant investigation by the United States Bureau of Mines showed that it was feasible to strip the precious metals from loaded charcoal with a solution of boiling caustic cyanide[4], the precious metals being recovered continuously from the concentrated stripping solution by electrolysis. The metallic gold and silver were recovered by the smelting of the cathode, which was made of stainless-steel wool. The stripped charcoal was re-used fifteen times, and the solution of caustic cyanide was regenerated and re-used ten times. The estimated cost of reagents, power, and stainless-steel wool, excluding the cost of heating, was about 63 U.S. cents per ounce of gold recovered[3].

The feasibility of using activated charcoal for the recovery of gold was greatly enhanced by the development of techniques that permitted the charcoal to be used again and again. However, the rate at which the precious metals could be stripped from the loaded charcoal was relatively slow. For example[5], at Homestake in the U.S.A., a period of 24 to 48 hours was required for the loaded charcoal to be stripped satisfactorily under plant conditions with a caustic cyanide solution at 93 °C. For the loaded charcoal to be stripped to less than 150 p.p.m. of gold in 2 to 6 hours, the stripping temperature and pressure had to be raised to 150 °C and 360 kPa respectively[5].

In recent years, faster stripping techniques have been developed at the Anglo American Research Laboratories (AARL) in South Africa[6, 7]. In 1976 a collaborative project involving the Vaal Reefs Exploration and Mining Company Limited, the AARL, and the National Institute for Metallurgy (NIM) was started. The project was sponsored partially by the Chamber of Mines of South Africa, and its main aim was the evaluation, on pilot-plant scale, of the technical and economic feasibility of a process that incorporates

(1) the adsorption of low concentrations of dissolved gold on activated charcoal in an upflow fluidized-bed column,
(2) the stripping of the loaded charcoal in a fixed-bed column by use of the techniques developed by AARL,
(3) the electrowinning of the gold from the concentrated stripping solution, and
(4) the thermal regeneration of the stripped charcoal before its return to the adsorption column.

The discussion in this paper is confined mainly to the adsorption stage of this process.

Some of the Properties of Activated Charcoal

Activated charcoals are produced commercially from a variety of carbonaceous materials. Nutshells, fruit pits, bituminous coal, and wood are some of the starting materials that are used in the production of activated charcoals suitable for the recovery of precious metals. Hard, abrasion-resistant charcoals like that produced from coconut shells are preferred in fluidized-bed columns and in carbon-in-pulp contactors. Some of the more important physical properties of coconut-shell charcoal are listed in Table I.

The adsorptive properties of activated charcoal are due to its highly reactive surface, and to its surface area and pore-size distribution.

*Formerly of the National Institute for Metallurgy, Randburg; now with the Fil-Tron Equipment Division, Davy Ashmore South Africa (Pty) Ltd, Johannesburg.

The reactivity of the surface arises largely from the many structural imperfections, which lead to many possible reactions between the edge carbons and functional groups at the surface and their surrounding species. The total surface area of granular activated charcoal produced from coconut shells is between 1150 and 1250 m^2/g.

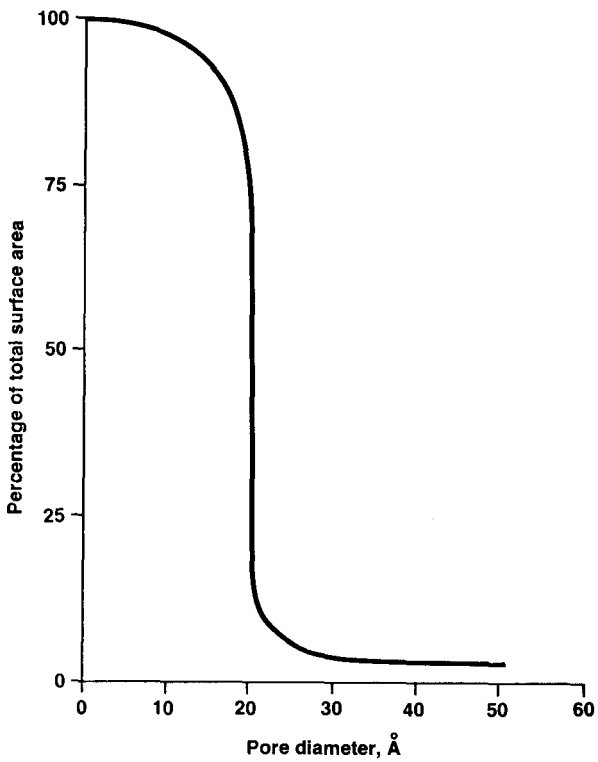

Fig. 1—The pore-size distribution in coconut-shell charcoal

TABLE I

SOME PHYSICAL PROPERTIES OF COCONUT-SHELL CHARCOAL

Total surface area (m^2/g)	1150 to 1250
Particle density (g/cm^3)	0,80 to 0,85
Real density (g/cm^3)	2,0 to 2,2
Bulk density (g/cm^3)	0,45 to 0,48
Pore volume within particle (cm^3/g)	0,70 to 0,80
Voids in packed bed (%)	38 to 42
Specific heat at 100°C (kcal/kg/°C)	0,20 to 0,25
Hardness number	95 to 99
Ash (%)	1 to 4

Notes

(a) The total surface area is determined from the BET[8] nitrogen isotherm.

(b) The particle density is determined by mercury displacement, and the real density by helium displacement.

(c) Hardness number is a measure of the resistance of the charcoal to degradation by the action of steel balls. It is twice the mass of charcoal, from an initial sample of 50 g, retained on a certain sieve after a standard test procedure.

The distribution of pore sizes in a typical granular coconut-shell charcoal is shown in Fig. 1. A large portion of the total surface area of each granule is occupied by micropores that are 18 to 21 Å in diameter. In addition, each granule is permeated by a system of gross pores (macropores), which serve as avenues for rapid diffusion.

The standard size ranges for coconut-shell charcoal are typically 0,6 to 1,7 mm, 1,2 to 3,4 mm, and 2,0 to 4,8 mm. The mean particle diameters in these three sizes of material are about 1 mm, 2 mm, and 3 mm respectively. Oversize granules do not exceed 10 per cent, and undersize granules represent 5 per cent or less, of the material.

The real density of cocnut-shell charcoal is 2,0 to 2,2 g/cm^3, and the volume of the pores within each

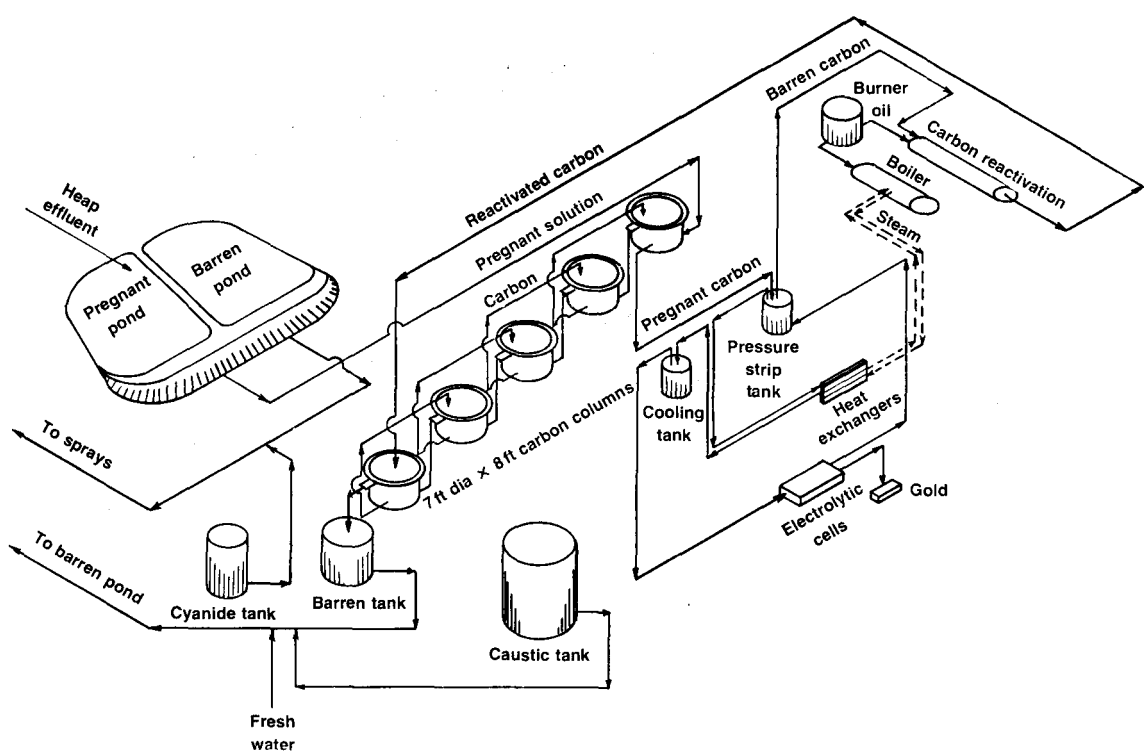

Fig. 2—The carbon-recovery circuit at Cortez Gold Mines

TABLE II

THE DETAILS OF TWO PLANTS OPERATING IN THE UNITED STATES

	Cortez	Smokey Valley
Number of adsorption vessels in series	5	5
Diameter of each adsorption vessel, m	2,13	3,66
Height of each adsorption vessel, m	2,44	2,44
Flow-rate of solution, l/min	2080	4540 to 6050
Superficial velocity of solution, m/h	34,9	25,9 to 34,6
pH value of leach liquor	10,5	9,5 to 10,5
Charcoal inventory in each adsorption vessel, kg	1360	3180
Expansion of charcoal bed, %	35	
Height of settled-charcoal bed*, m	0,85	
Height of expanded-charcoal bed*, m	1,14	
Flow-rate of charcoal, kg/d	545	909
Ratio of solution flow-rate to charcoal flow-rate	5500:1	7200:1 to 9600:1
Mean residence time of charcoal, d	12,5	17,5
Gold concentration in feed solution, p.p.m.	0,60	
Gold concentration in barren solution, p.p.m.	0,014	
Gold concentration on loaded charcoal, p.p.m.	13760	7090
Gold concentration on stripped charcoal, p.p.m.	11	

*These values are calculated at a bulk relative density of 0,45 (see Table I).

particle is 0,70 to 0,80 cm^3/g (Table I). When these pores are filled with water, the density of the particle is 1,38 to 1,47 g/cm^3.

Activated Charcoal in Fluidized-bed Contactors

Activated charcoal is at present being used in fluidized-bed contactors for the adsorption of dissolved gold in unclarified solutions from dump-leach plants at Cortez Gold Mines and Smoky Valley Mining in the U.S.A.[9, 10]. The details of the adsorption operations at these mines are given in Table II, and the flowsheet of the recovery circuit at Cortez Gold Mines is shown in Fig. 2.

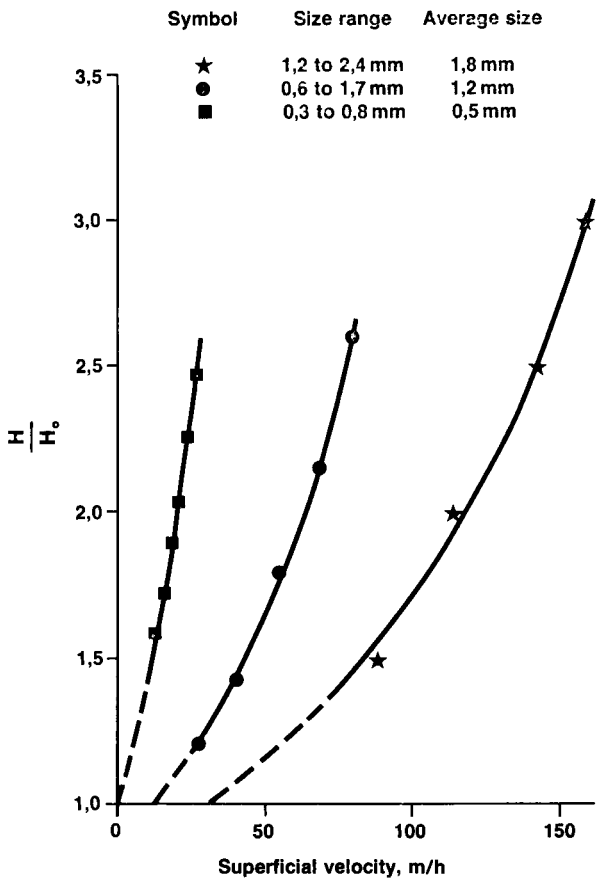

Fig. 3—The bed expansion of coconut-shell charcoal in water

In the adsorption section at Cortez, coconut-shell charcoal in the size range 0,6 to 1,7 mm is used in the five fluidized-bed contactors. The solution from the dump-leach plant is pumped into the bottom of the first stage and is distributed by a number of nozzles at the base of the adsorption vessel. The five stages are arranged so that the solution leaving the top of the first stage can be fed under gravity into the bottom of the second stage, and so on. The solution is redistributed at the bottom of each vessel, and eductors are used to move slugs of charcoal countercurrent to the flow of solution.

The superficial flow velocity of the solution in the adsorption vessels at Cortez Gold Mines is 34,9 m/h, and the charcoal bed expands by 35 per cent at that velocity. The heights of the settled and expanded beds of charcoal in each stage are 0,85 and 1,14 m respectively. Of the total charcoal inventory, 8 per cent is moved countercurrent to the solution each day, and the residence time of the charcoal in the adsorption circuit is therefore 12,5 days.

These details of the adsorption circuit illustrate some of the more important design and operating parameters of countercurrent fluidized-bed contactors. The details do not, however, give an indication of the possible range of superficial velocities when activated charcoal is used as the solid adsorbent in the contactor.

The flow-rate of the solution through a fluidized bed is limited on the one hand by the minimum fluidization velocity, U_{mf}, and on the other hand by the velocity at which particles of solid adsorbent are entrained in the solution leaving the contactor. This upper limit to the flow-rate of solution can be approximated by the free-fall velocity of the smallest solid particles in the fluidized bed.

The bed-expansion curves for three size ranges of granular coconut-shell charcoal in water as determined from fluidization experiments in the laboratory are shown in Fig. 3. The bed expansion is expressed in terms of H/H_0, where H and H_0 are the heights of the expanded and the wet-settled beds respectively. The experimental curves were extrapolated to intersect the abscissa at the calculated values of the minimum fluidization velocity[11], and show that a bed expansion of 100 per cent is achieved at superficial velocities of

20, 63, and 118 m/h for the three different sizes of charcoal.

The combined effects of the density and viscosity of the fluidizing medium on the bed expansion of coconut-shell charcoal in the size range 1,2 to 2,4 mm is shown in Fig. 4. As shown there, the superficial velocity of a solution of calcium nitrate (relative density 1,29 and relative viscosity 5,5) for a bed expansion of 100 per cent is 81 m/h, while that of water is 118 m/h.

The density of a suspension of fine silica particles (20 per cent by mass) in water is 1,14 g/cm³. According to the results obtained at NIM, the viscosity of this suspension relative to water at the same temperature, μ^*, can be calculated from the following relationship:

$$\mu^*=(1-X)^{-2,35},$$

where X=mass fraction of silica.

If X is 0,20, the relative viscosity is 1,69. The relative density (1,14) and the relative viscosity (1,69) of the suspension are well within the values for the calcium nitrate solution shown in Fig. 4 (1,29 and 5,5 respectively). A bed of coconut-shell charcoal in the size range 1,2 to 2,4 mm could thus be expected to expand by 100 per cent in this suspension at a superficial velocity of between 81 and 118 m/h.

The free-fall velocities of spherical particles are given by the following expressions[11]:

$$U_t=\frac{g(\rho_s-\rho)d^2}{18\mu} \text{ for } Re_p<0,4 \quad \ldots\ldots\ldots \text{(A)}$$

$$U_t^3=\frac{4g^2(\rho_s-\rho)^2d^3}{225\rho\mu} \text{ for } 0,4<Re_r<500 \quad \ldots\ldots \text{(B)}$$

The size of a spherical silica particle (relative density 2,7) that has a free-fall velocity of 81 m/h (2,25 cm/s) in water, is 132 μm from Equation (B). In a suspension of silica particles in water, the free-fall velocity of a particle of diameter 132 μm would be less than 2,25 cm/s because

(a) the grains of silica are not spherical, and
(b) there is mutual interference in the motion of the particles, resulting in 'hindered' and not 'free' settling conditions.

In practice, therefore, it should be possible to pass a suspension of silica particles having diameters greater than 132 μm through a fluidized bed of coconut-shell charcoal in the size range 1,2 to 2,4 mm at a superficial velocity of 81 m/h. Similar estimates can be made for other size ranges of coconut-shell charcoal at different superficial velocities of the fluidizing medium.

Pilot Plant at Vaal Reefs

The flowsheet of the pilot plant that was erected at Vaal Reefs North (West Section) is shown in Fig. 5.

The adsorption contactor was a continuous ion-exchange contactor of the NIMCIX type, which was originally developed by NIM and the Extraction Metallurgy Division of the Atomic Energy Board for the recovery of uranium from unclarified leach liquors. The adsorption column was 0,6 m in diameter and contained approximately 750 kg of coconut-shell charcoal in the size range 1,2 to 2,4 mm. The total expanded height of the charcoal bed was 6 m at a solution superficial velocity of 21,2 m/h (5,9 cm/s).

After a week of continuous adsorption, 100 kg of loaded charcoal was extracted from the bottom stage of the NIMCIX column, and 100 kg of stripped and thermally regenerated charcoal was added to the top stage. The average residence time of the charcoal in the adsorption column was therefore approximately 50 days. The flow-rate of solution to the flow-rate of charcoal was in a ratio of approximately 10^4 to 1. The unclarified feed solution to the column had a pH value of 10,5 to 11,5, and the dissolved gold it contained had an average concentration of approximately 0,2 p.p.m.

The percentage recovery of dissolved gold in the adsorption column decreased from over 90 per cent at the outset to as little as 50 to 60 per cent by the end of the seventh week of operation. During this period of operation, calcium was being loaded on the charcoal at the rate of approximately 0,57 per cent by mass per week, so that, at the end of seven weeks, the loaded charcoal was contaminated with nearly 4 per cent by mass of calcium. The charcoal was then washed with dilute hydrochloric acid at the end of each adsorption cycle, and there was a gradual decline in the recovery of dissolved gold from the start of the next adsorption cycle until the next acid wash: the average concentration of dissolved gold in the solution from the NIMCIX column during a single adsorption cycle of one week was 0,01 p.p.m. (at a head value of approximately 0,2 p.p.m.), and the concentration was as low as 0,003 p.p.m. during the first day of the adsorption cycle after the acid wash. (The concentration of dissolved gold in the feed and barren solutions was determined by atomic-absorption spectrophotometry.)

The concentration of gold on the loaded and stripped charcoals was approximately 2000 p.p.m. and 100 p.p.m. respectively. When the adsorption cycle and the mean residence time of the charcoal in the adsorption column were doubled from 7 and 50 days to 14 and 100 days respectively, there was an increase in the gold loaded on the charcoal, but the concentration of dissolved gold in the barren solution also increased significantly.

The operation of the NIMCIX contactor was found to be stable when granular activated charcoal was used as the solid adsorbent in the contacting stages. The loaded charcoal was transported successfully between the bottom of the column and the transfer vessel during the reverse-flow and delay periods, in the operating cycle of the contactor, as was the loaded charcoal between the transfer vessel and the stripping column.

Conclusions

Coconut-shell charcoal in the size range 1,2 to 2,4 mm was shown to be an excellent scavenger for dissolved gold present in low concentrations in an alkaline cyanide solution. The average concentration of dissolved gold in the solution from a NIMCIX contactor was maintained at 0,01 p.p.m. under the following operating conditions on the pilot plant:

(1) approximately 0,2 p.p.m. of dissolved gold in the feed solution,
(2) treatment of the charcoal in the adsorption column at least once per week with dilute hydrochloric acid,

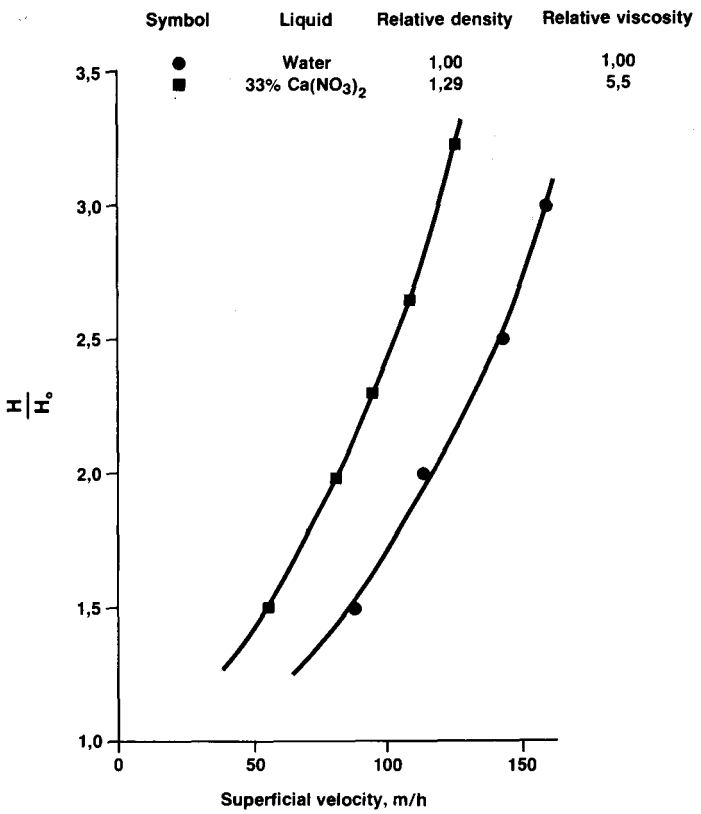

Fig. 4—The combined effects of solution density and viscosity on the bed expansion of coconut-shell charcoal

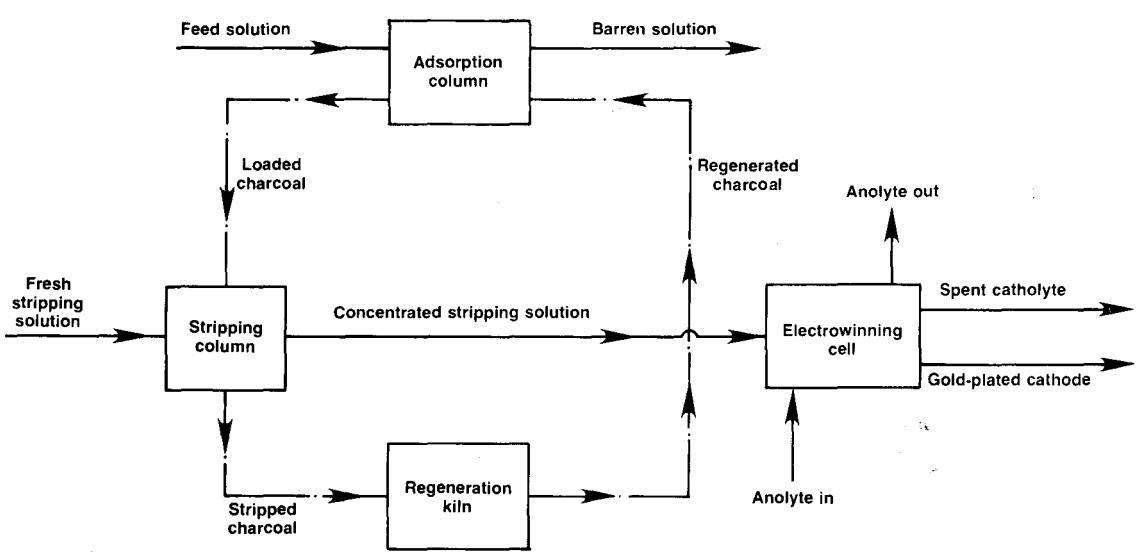

Fig. 5—The flowsheet of the pilot plant at Vaal Reefs

(3) an adsorption cycle of no longer than seven days and a mean residence time for the charcoal in the adsorption column of no more than 50 days,
(4) a superficial velocity of no more than 21,2 m/h, and
(5) an expanded bed height of at least 6 m.

Coconut-shell charcoal is ideally suited for use in a NIMCIX contactor. Because of the wide range (0,3 to 4,8 mm) of available particle sizes, a large range of superficial velocities is possible. Relatively high superficial velocities can be attained owing to the high relative density of the material and the size of the granules in comparison with standard column-grade ion-exchange resins. It is theoretically possible to pass relatively coarse particles, of approximately 150 μm in diameter, through the fluidized bed in the column. Coconut-shell charcoal is relatively hard and resistant to abrasion, and granular charcoal can be readily transported under hydraulic pressure.

Acknowledgements

This paper is published by permission of the National Institute for Metallurgy and the Chamber of Mines of South Africa on behalf of the sponsors of this research programme.

References

1. DAVIS, W. M. Use of carbon for the precipitation of gold from solution and subsequent burning. *U.S. Patent* 227963, 25th May, 1880.
2. GROSS, J., and SCOTT, J. W. Precipitation of gold and silver from cyanide solution on charcoal. U.S. Bureau of Mines, *Technical Paper* 378. 1927.
3. GILMORE, A. J. A proposed method for gold recovery from flotation plant effluents with activated charcoal. *Can. Min. J.*, vol. 90. Jun. 1969. pp. 78-80.
4. ZADRA, J. B., *et al.* Process for recovering gold and silver from activated carbon by leaching and electrolysis. U.S. Bureau of Mines, *R.I.* 4843. Feb. 1952.
5. POTTER, G. M., and SALISBURY, H. P. Innovations in gold metallurgy. *Mining Cong. J.*, vol. 60. Jul. 1974. pp. 54-57.
6. DAVIDSON, R. J. The mechanism of gold adsorption on activated charcoal. *J. S. Afr. Inst. Min. Metall.*, vol. 75, no. 4. Nov. 1974. pp. 67-76.
7. DAVIDSON, R. J., and DUNCANSON, D. The elution of gold from activated carbon using de-ionized water. *J. S. Afr. Inst. Min. Metall.*, vol. 77, no. 12. Jul. 1977. pp. 254-261.
8. BRUNAUER, S., EMMETT, P. H., and TELLER, E. *J. Am. Chem. Soc.*, vol. 60. 1938. p. 309.
9. DUNCAN, D. M., and SMOLIK, T. J. How Cortez Gold Mines heap-leached low-grade gold ores at two Nevada properties. *Engng Min. J.*, vol. 178, no. 7. Jul. 1977. pp. 65-69.
10. WHITE, L. Heap leaching will produce 85 000 oz/year of dore bullion for Smoky Valley Mining. *Engng Min. J.*, vol. 178, no. 7. Jul. 1977. pp. 70-72.
11. KUNII, D., and LEVENSPIEL, O. *Fluidization engineering.* New York, John Wiley, 1969. pp. 72-79.

Courses on geostatistics

In view of the continuing demand, the Department of Mining and Mineral Sciences of the University of Leeds, in association with Special Courses Division, Department of Adult Education and Extramural Studies, will offer two further courses entitled 'A practical introduction to geostatistics'. The courses, each of which covers ten working days, will be held at the University from 9th to 22nd April, 1980, and from 15th to 26th September, 1980.

The programme for each of the courses will be as follows:

First week

Monday	Historical introduction and review of recommended reading
	The semi-variogram
	Volume–variance relationship
	Krige's formula
	Variances of distribution
	Grading and regularization
Tuesday	Estimation of area
	Intrinsic schemes
	Fitting models to semi-variograms
Wednesday	Extension variance
	Variances of estimation
Thursday	Sampling patterns
	Estimation of total ore reserves
Friday	Location estimation
	Estimation of stoping blocks
	Kriging

Second week

Monday	Kriging (continued)
	Sampling distributions and block value distributions
Tuesday	Elementary kriging
	Random kriging
Wednesday	Proportional effects
	Compound variograms
Thursday	Daily variation in mined grade
	Grade–tonnage curves
Friday	Completion of exercises
	Resumé and discussion.

Further information is obtainable from The Director of Special Courses, Department of Adult Education and Extramural Studies, The University, Leeds LS2 9JT, England.