

The regeneration of activated carbon

by B.M. VAN VLIET*

SYNOPSIS

This paper outlines the principles involved in the regeneration of activated carbon for renewed use in the recovery of precious metals or the purification of water. While chemical methods are effective in restoring the activity of spent activated carbon containing only single or defined adsorbates, thermal methods have to be used when the spent carbon is loaded with a heterogeneous mixture of adsorbates such as those normally present in industrial process streams or effluents. The steps involved in thermal regeneration are described, together with the operating conditions that can be controlled to give the required degree of activation. Finally, an account is given of the structural changes that occur in a new or spent activated carbon during thermal treatment.

SAMEVATTING

Hierdie referaat bespreek in hoofreкке die beginsels betrokke by die regenerering van geaktiveerde koolstof vir hernieuwe gebruik in die herwinning van edelmetale of die suiwering van water. Terwyl chemiese metodes doeltreffend is om die aktiwiteit van uitgewerkte koolstof met net enkele of omskrewe adsorbate te herstel, moet termiese metodes gebruik word wanneer die uitgewerkte koolstof gelaai is met 'n heterogene mengsel van adsorbate soos dié wat gewoonlik in nywerheidsprosesstrome of -uitvloeiels aanwesig is. Die stappe betrokke by termiese regenerasie word beskryf, tesame met die bedryfstoeistande wat beheer kan word om die vereiste graad van aktivering te gee. Ten slotte word die strukturele veranderinge bespreek wat tydens die termiese behandeling in 'n nuwe of uitgewerkte koolstof plaasvind.

Introduction

The economic feasibility of processes using granular activated carbon for the recovery of precious metals or the purification of water and waste-water is contingent upon re-use of the carbon in multiple adsorption-regeneration cycles. Different techniques can be used to restore the activity of a spent (exhausted) activated carbon.

- Chemical techniques involve treatment of the carbon by solvent extraction with acids or alkalis, or by combinations of such treatments¹⁻³. Picht *et al.*⁴ successfully used supercritical carbon dioxide as a solvent and, more recently, Slavinskii *et al.*⁵ reported their use of electrochemical regeneration techniques.
- Regeneration by thermal techniques involves the use of rotary kilns, fluidized-bed furnaces, multiple-hearth furnaces, electrical resistance furnaces, conveyor-belt furnaces, indirect heating furnaces, and other types of equipment.

Various chemical methods can effectively restore the activity of spent carbon from which only single or defined adsorbates need to be removed or recovered. In such cases, appropriate solvents and/or chemicals are used to specifically desorb the adsorbates in question. However, chemical regeneration can restore only partial activity to carbon that is loaded with a heterogeneous mixture of adsorbates such as those normally present in industrial process streams or effluents⁶. Davidson and Tumilty⁷ have pointed out that, while chemical regeneration may restore sufficient activity to the carbon for a few cycles of effective operation, comprehensive thermal regeneration must be applied at regular intervals to restore com-

plete activity. Thermal regeneration effectively restores the activity of carbons loaded with organic adsorbates.

Principles of Regeneration

During adsorption, many organic and inorganic adsorbates can accumulate within the porous structure of activated carbon. Micropores (up to 3 nm) constitute the primary adsorption sites, and therefore tend to become congested to a greater degree than do mesopores (3 to 60 nm) and macropores (60 to 10 000 nm). However, mesopores and macropores also capture adsorbates of relatively high molecular mass and, as a result, there is a progressive decline in adsorption efficiency. Activated carbon that is used to purify water upstream of a carbon-in-pulp (CIP) process—by capturing organic compounds that are likely to foul the carbon in the CIP reactors—needs periodic thermal treatment to selectively remove the organic adsorbates and thus restore its activity. In a CIP arrangement that does not include adsorptive pretreatment, organic adsorbates can be partially desorbed during the elution of the precious metals from the carbon (including pretreatment with hot acid), but a substantial fraction of these adsorbates will remain and will have to be dealt with at regular intervals by thermal treatment.

The objectives during regeneration are the selective removal of the adsorbates that have accumulated on the carbon during adsorption operations, and the restoration of the original porous structure and activity of the carbon with as little damage as possible to the carbon itself. This paper focuses on the removal of organic adsorbates from spent activated carbon.

Regeneration Steps

The following steps are usual in the thermal regeneration of a spent carbon:

* CSIR Division of Water Technology, P.O. Box 395, Pretoria 0001.
© The South African Institute of Mining and Metallurgy, 1991. SA ISSN 0038-223X/3.00 + 0.00. Paper received 1st November, 1989.

- (a) drying, which eliminates the highly volatile adsorbates (at temperatures of up to about 200°C),
- (b) vaporization of the volatile adsorbates, and decomposition of the unstable adsorbates to form volatile fragments (from about 200 to 500°C),
- (c) pyrolysis of the non-volatile adsorbates (at about 500 to 700°C), which results in the deposition of a carbonaceous residue on the surface of the activated carbon, and
- (d) selective oxidation of the pyrolysed residue (at about 700°C and higher) by steam, carbon dioxide, any other oxidizing agent, or any combination of the foregoing.

The first three steps, viz drying, vaporization, and pyrolysis, normally proceed with few complications. However, pyrolysis should not be conducted at temperatures higher than 850°C in a non-oxidizing atmosphere, since graphitization of the pyrolysed residue can occur, resulting in a structure similar to that of activated carbon and equally refractive. Hence, during subsequent selective oxidation, it would be difficult to remove the residue without extensively damaging the structure of the activated carbon. Pyrolysed residues obtained at lower temperatures are reported to be more reactive, and therefore more readily oxidizable, than activated carbon⁸.

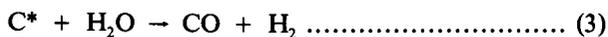
The proper reactivation of carbon does not involve direct oxidation of the pyrolysed residue with oxygen. On the contrary, the atmosphere within that zone of the furnace is deliberately depleted in oxygen so that the following reactions will be minimized:



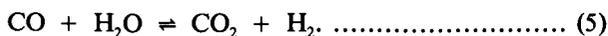
where C* denotes the carbonaceous pyrolysed residue or the structure of the activated carbon.

Since these reactions are exothermic, and therefore self-promoting, they would, if allowed to occur, result in aggressive oxidation along the surface of the carbonaceous residue and of the original activated carbon. In practice, this would have the following effects. The pores would widen, the residue would not be removed from deep pores and, in general, the adsorption sites would not be reactivated. The result would be excessive losses of valuable activated carbon.

In an atmosphere consisting of steam or carbon dioxide (besides nitrogen, which may also be present), the following endothermic reactions will predominate:



An input of energy is required to sustain these endothermic reactions, which constitute the principal reactions that can be effectively controlled in the oxidation and gasification of pyrolysed adsorbate with minimal damage to the structure of the activated carbon. Reaction (3) and the gas-phase reaction



constitute the overall steam-carbon (water-gas) reaction that will predominate when the partial pressure of carbon dioxide, p_{CO_2} , p_{H_2} , is low compared with that of steam.

The composition of the gas phase shifts towards equilibrium in accordance with equation (5). The equilibrium constant⁹, is

$$K = \frac{p_{CO_2} \cdot p_{H_2}}{p_{CO} \cdot p_{H_2O}} \dots\dots\dots (6)$$

$$= 1 \text{ at } 870^\circ\text{C},$$

where p denotes partial pressure.

Response of Different Compounds to Thermal Regeneration

In thermal regeneration, the adsorbates associated with a spent carbon can be conveniently classified according to their responses, which are of the following types.

Type I

Volatile organic compounds that were initially adsorbed onto the activated carbon but were not irreversibly bound to active surface sites undergo thermal desorption.

Type II

Organic compounds that are not sufficiently volatile for thermal desorption, and/or that are tenaciously bound to surface sites, undergo thermal decomposition (cracking) and form volatile fragments.

Type III

The remaining compounds are pyrolysed, and a carbonaceous residue is deposited concomitantly at about 800°C. Compounds that participate in this type of reaction are most critical in the regeneration process, since the carbonaceous residue has to be removed selectively, through endothermic oxidation with steam or carbon dioxide, at comparatively high temperatures (above 800°C). Within this temperature domain, losses of energy increase significantly, equipment specifications become more stringent and equipment more costly, and losses of the activated-carbon backbone invariably occur concomitantly with the oxidation of the pyrolysed adsorbate residues.

In reality, many organic adsorbates display different combinations of Types I to III behaviour. Urano *et al.*¹⁰ analysed thermogravimetric curves for various pure (single-component) adsorbates on activated carbon, and classified them (Table I).

Suzuki *et al.*¹¹ classified organic adsorbates in a similar fashion (Table II), and considered the possible influence of various properties of the adsorbates (boiling point, aromaticity, oxygen content, molecular mass, and chemical functional groups) on their response to thermal treatment. Boiling point and aromaticity (i.e. ratio of aromatic carbon atoms to total carbon atoms in a molecule) appear to characterize most significantly the behaviour of an adsorbate during (inert) thermal treatment, in particular the extent to which carbonaceous residuals are deposited upon heating to 800°C. Organic compounds with high boiling points and of appreciable aromatic content are likely to exhibit Type III behaviour with substantial carbonaceous residuals at 800°C. Prime examples of such intractable adsorbates are humic acids (which are ubiquitous in water supplies), lignin, phenol, and substituted phenols.

Thermal analysis techniques have been used to charac-

TABLE I
RESPONSE OF SELECTED ADSORBATES TO THERMAL TREATMENT (AFTER URANO *ET AL.*¹⁰)

Adsorbate	Molecular mass	Boiling point °C	Aromaticity*	Carbonaceous residual† fraction at 700°C	Response to thermal treatment (under N ₂)
Toluene	92	111	0,86	0	Type I: completely vaporized or sublimated until about 300°C
Nitrobenzene	121	211	1,00	0	
Propionic acid	74	141	0,00	0,01	Types I, II, and III: desorbed partially by vaporization and thermal decomposition, with some carbonaceous residue at 700 °C
Benzoic acid	122	249	0,86	0,03	
Salicylic acid	139	256	0,86	0,13	
Aniline	93	185	1,00	0,34	
Phenol	94	180	1,00	0,36	
Chlorophenol	129	214	1,00	0,40	
Nitrophenol	139	215	1,00	0,34	
Resorcinol	110	277	1,00	0,50	
2-naphthol	144	288	1,00	0,62	
Benzene sulphonic acid	156	—	1,00	0,36	
Dodecyl benzene-sulphonic acid	348	—	0,33	0,30	Types II and III: desorbed partially by thermal decomposition, leaving carbonaceous residue at 700 °C

* Ratio of aromatic-to-total carbon atoms in molecule

† The fraction of the original adsorbate remaining as carbonaceous residual at 700°C under N₂; estimated from figures presented by Urano *et al.*¹⁰; heating rate 17°C/min

TABLE II
RESPONSE OF SOME SELECTED ADSORBATES TO THERMAL TREATMENT (AFTER SUZUKI *ET AL.*¹¹)

Adsorbate	Molecular mass	Boiling point °C	Aromaticity*	Carbonaceous residual† fraction at 800°C	Response to thermal treatment (under N ₂)
n-pentane	72	36	0,00	0,00	Essentially Type I (vaporization or sublimation) with little or no residue upon heating to 800 °C
n-hexane	86	69	0,00	0,00	
n-heptane	100	98,4	0,00	0,00	
n-decane	142	174	0,00	0,00	
Benzene	78	80	1,00	0,00	
Toluene	92	110,6	0,86	0,00	
p-xylene	106	114	0,75	0,03	
Butyric acid	88	164,1	0,00	0,01	
Butanol	74	118,0	0,00	0,02	
Hexanol	102	157,5	0,00	0,04	
Octanol	130	194,5	0,00	0,03	
Tetraethyleneglycol	194	—	0,00	0,00	Essentially Type II (thermal decomposition), with little or no residue upon heating to 800 °C
Caproic acid	116	205,4	0,00	0,04	
Benzoic acid	122	250	0,86	0,15	Essentially Type III, with high residue upon heating to 800 °C
Humic acid	—	—	—	0,26	
p-oxybenzaldehyde	122	310	0,86	0,35	
Lignin‡	165	—	0,60	0,45	
p-hydroxydiphenyl	170	308	1,00	0,49	
Methylene blue	320	—	0,38	0,58	
Phenol	94	182	1,00	0,61	
β-naphthol	144	285	1,00	0,68	

* Ratio of aromatic-to-total carbon atoms in molecule

† The fraction of the original adsorbate remaining as carbonaceous residual at 800°C under N₂; heating rate 6°C/min

‡ Soft wood (coniferous), monomeric unit¹²

terize the response to thermal treatment of adsorbates on spent activated carbons¹³. This approach allows the amounts of adsorbates that will be removed within zones of increasing temperatures, as well as the amount of pyrolysed residue that will have to be selectively oxidized, to

be quantified.

Fig. 1 depicts the thermal-response distribution of the adsorbates for a spent carbon made from bituminous coal that had been used in the renovation of waste water and for spent coconut-shell carbon that had been used in a

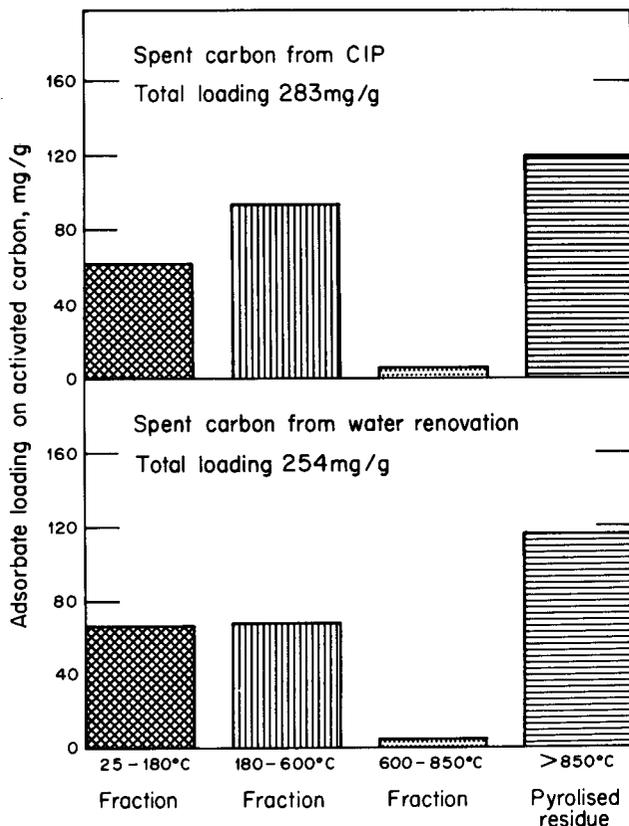


Fig. 1—Response of adsorbate to thermal treatment of spent activated carbons from water-renovation and CIP applications

CIP application. It can be seen that the distribution patterns are substantially the same for the two carbons, suggesting that similar regeneration requirements would pertain in each instance. The volatilization, decomposition, and pyrolysis of the adsorbates would approach completion at 600°C, with only a small measure of additional pyrolysis between 600 and 800°C. However, in both instances, there is a considerable amount of carbonaceous residue, which would require removal by selective oxidation. The pyrolysed residues as percentages of the total adsorbate loadings were 46 per cent for water renovation and 43 per cent for CIP.

If carbon were re-used after pyrolysis alone and the selective-oxidation step were omitted, progressive build-up of the pyrolysed residues would occur, with a concomitant decline in adsorption efficiency. Umehara *et al.*¹⁴, measuring the adsorption capacity of samples of regenerated carbon, found that thermal volatilization, decomposition, and pyrolysis alone resulted in a considerable loss (35 per cent) in adsorption capacity for sodium dodecylbenzene sulphonate (DBS). The thermal treatment described above, followed by steam oxidation of the pyrolysed residue, could completely restore the adsorption capacity for DBS on the remaining activated carbon.

Regeneration Conditions

Operating conditions during regeneration can be controlled to effect the required degree of regeneration of a spent carbon. The following parameters have an important influence on regeneration: furnace atmosphere, presence of inorganic constituents, and temperature and residence time.

Furnace Atmosphere

Thermal applications that employ the use of partial or complete steam atmospheres are examined here because this is the approach most commonly applied. The rule-of-thumb guideline of 1 kg of steam per kilogram of activated carbon has often been advanced as the requirement for the complete regeneration of spent carbon. In reality, the quantity of steam required depends on the kinetics of selective oxidation (gasification) of the pyrolysed residue.

Umehara *et al.*¹⁴ studied the kinetics of the reaction of steam with activated carbon containing a pyrolysed residue of DBS (a synthetic detergent) at 700 to 789°C and atmospheric pressure, and obtained data for different concentrations of steam and hydrogen. The results fitted a Langmuir-Hinshelwood rate equation, which had been developed originally for the oxidation of other types of carbon with steam¹⁵. According to that formulation, equation (7) expresses the effect of the concentrations of hydrogen and steam on the gasification rate for a fixed initial loading of adsorbate. (The initial DBS loading on the carbon was 0,522 g/g, and 45 per cent of this initial loading remained on the carbon as a non-volatile pyrolysed residue, which had to be selectively oxidized.)

$$R = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2} + k_3 P_{H_2O}}, \dots\dots\dots (7)$$

where

R is the reaction rate of steam gasification, i.e. the kilograms of carbon residue burned per second per kilogram of virgin carbon in existence when the sample reaches the reaction temperature, kg/(kg.2)

k_1 is the rate constant for the steam-gasification reaction, kg/(kg.s.Pa)

k_2 and k_3 are rate parameters, Pa⁻¹

P_{H_2O} and P_{H_2} are the partial pressures of steam and hydrogen respectively, Pa.

The values of the kinetic constants k_1 , k_2 , and k_3 as determined by Umehara *et al.*¹⁴ are presented in Table III.

The temperature dependence of the above kinetic coefficients was also delineated, and is described by the following set of equations:

$$k_1 = 1,02 \times 10^2 \exp(-E_1/RT), \text{ kg/(kg.s.Pa)} \quad (8)$$

$$k_2 = 1,02 \times 10^2 \exp(-H_2/RT), \text{ Pa}^{-1} \dots\dots\dots (9)$$

$$k_3 = 1,18 \times 10^{-3}, \text{ Pa}^{-1}, \dots\dots\dots (10)$$

where E_1 is the activation energy for rate constant k_1 , = 1,64 × 10⁵ J/mol,

H_2 is the enthalpy of adsorption for hydrogen = -1,70 × 10⁵ J/mol,

R is the gas constant, J/(mol.K), and T is temperature, K.

On the basis of equations (7) to (10), the oxidation rates were calculated as a function of temperature and steam concentration, and are presented in Figs 2 and 3. Although these values pertain to studies of a single adsorbate (DBS), it is an adsorbate that can be regarded as a typical organic contaminant of aromatic, aliphatic, and inorganic character. Its behaviour upon pyrolysis is similar to that of adsorbates derived from waste water

TABLE III
KINETIC CONSTANTS FOR STEAM-GASIFICATION REACTION (AFTER UMEHARA *ET AL.*¹⁴)

Temperature	700°C	729°C	759°C	789°C
k_1 , kg/(kg.s.Pa)	$1,59 \times 10^{-7}$	$2,66 \times 10^{-7}$	$5,36 \times 10^{-7}$	$8,70 \times 10^{-7}$
k_2 , Pa ⁻¹	$6,66 \times 10^{-3}$	$4,70 \times 10^{-3}$	$2,60 \times 10^{-3}$	$1,48 \times 10^{-3}$
k_3 , Pa ⁻¹	$1,27 \times 10^{-3}$	$1,17 \times 10^{-3}$	$1,13 \times 10^{-3}$	$1,13 \times 10^{-3}$

and CIP in that it deposits a substantial non-volatile carbonaceous residue and a small inorganic (Na₂SO₄) residue.

Fig. 2 shows that at all temperatures the reaction rate (R) is particularly sensitive to dilute concentrations of steam (below about 20 mol per cent) in the reactivating gas.

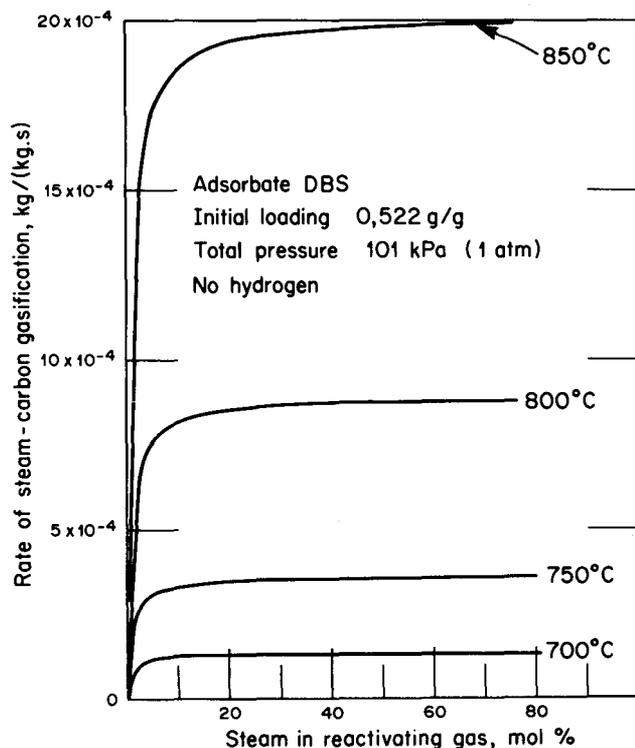


Fig. 2—Steam-gasification rate of pyrolysed residue as a function of temperature and steam concentration

Hydrogen, which—as shown by equations (3) and (5)—is a byproduct of the reactivation reaction, will naturally tend to suppress the reaction rate (R) via the reaction shown in equation (7), and will also extend the concentration range within which R will be sensitive to the steam level. Nevertheless, the reaction rate levels off, and is relatively insensitive to further increases in the concentration of steam above about 25 per cent.

Fig. 3 illustrates the temperature dependence of the steam-carbon gasification rate for DBS. It can be seen that the reaction rate is negligible at 650°C, reaches a practical level at 700°C, and subsequently virtually doubles for every 50°C increase in temperature.

The rate of the steam-carbon reaction is likely to be the controlling step in the selective oxidation of carbonized adsorbate residues. Chihara *et al.*¹⁶ demonstrated that intraparticle diffusion is not likely to affect the over-

all kinetics of regeneration at the temperatures normally employed in such operations. Also, Klei *et al.*¹⁷ reported that the steam-carbon reaction is relatively insensitive to the flowrate of gas (steam) around the particles, and that therefore the external mass-transfer rate does not control the overall reaction dynamics.

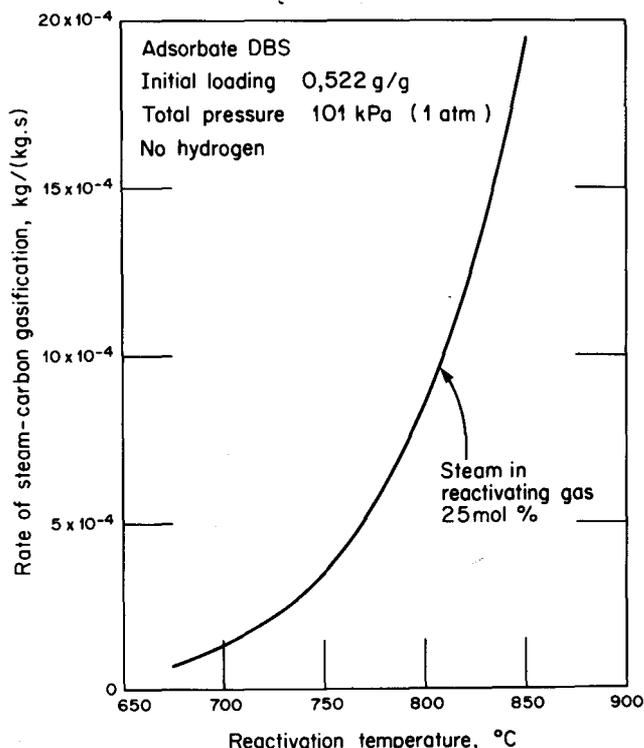


Fig. 3—Steam-gasification rate of pyrolysed residue as a function of temperature

Influence of Inorganic Constituents

Various inorganic constituents can catalyse the steam-carbon reaction, and can therefore accelerate the gasification of pyrolysed adsorbate residues, or even of base activated carbon. Such inorganic constituents can be present in the original structure of activated carbon, be adsorbed onto the carbon during usage, or be intrinsic parts of organic adsorbates. In the last-mentioned case, a non-volatile inorganic residue will be deposited, together with the carbonaceous residue, during the pyrolysis step of thermal-regeneration operations.

Umehara *et al.*¹⁴ have shown that an inorganic residue (sodium sulphate), which is deposited during the carbonization of a DBS-loaded carbon, exerts a substantial catalytic effect on the subsequent steam-motivated gasification of the carbonaceous residue. They obtained their evidence by measuring the rates of gasification for

virgin carbon that had adsorbed various amounts of sodium sulphate before being regenerated, and for DBS-loaded samples containing different amounts of inorganic residue. In both types of experiment, the rate was found to increase with the amount of inorganic material present.

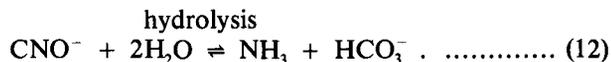
The rate of gasification was approximately the same when the samples contained the same fraction of inorganic material, either as added sodium sulphate (to virgin carbon) or as inorganic residue in the DBS-loaded samples. Furthermore, the reaction rate for thermally regenerated samples was reduced significantly by washing with water (which dissolves some of the inorganic material), followed by gasification with steam. These findings agree with those of McKee¹⁸, who demonstrated the catalytic effect of sodium on the gasification rate of carbon. Smisek and Cerny¹⁹ listed oxides and carbonates of alkali metals (such as sodium and potassium), iron, and copper as catalysts that have an impact on the activation or reactivation of carbon.

Juhola²⁰ reported that the ash content of granular carbon increases with each successive cycle of adsorption-regeneration, so that the amount of steam required to regenerate the carbon to its initial bulk density has to be decreased substantially. He concluded that the increase in the ash content of the carbon had catalysed the oxidation of the carbon's basic structure in such a manner as to reduce its adsorptive capacity. The ash included materials such as the oxides of iron, calcium, magnesium, potassium, sodium, and chromium. Pretreatment of the carbon with acid reduced the ash content of the carbon and minimized deterioration of the structure of the activated carbon during regeneration.

Harriott and Cheng²¹ showed that the minerals present in activated carbons can change the reactivity of the carbons and of the pyrolysis residues. For example, for spent carbons prepared by the adsorption of sodium benzoate onto the carbon and pyrolysis at 700°C, the reactivity to oxygen increased with the amount of residue produced. Even when the residue represented only 5 per cent by mass of the base carbon, the rate was 3,5 times that for the (base) carbon. Similarly, Prodan *et al.*²² showed that metal oxides in activated carbons catalyse the oxidation of adsorbed organic compounds, thus permitting the temperature of thermal regeneration to be reduced from 800 to 350°C. The same authors²³ and Mamontova *et al.*²⁴ substantiated the catalytic role of inorganic compounds during regeneration.

In the recovery of adsorbed gold, washing of the carbon with hot dilute hydrochloric acid prior to elution of the gold by the AARL procedure is far preferable if overall plant efficiency is to be maintained⁷. Besides the capacity of activated carbon to adsorb a substantial amount of acid, the requirements for acid washing will depend on the calcium carbonate content of the carbon. In most instances the use of approximately 1 bed volume of hydrochloric acid at a concentration of 3 per cent by volume is reported to effectively remove calcium from a loaded carbon. Dilute acid will effectively remove calcium and zinc from carbon, but hot acid at about 90°C will remove calcium, zinc, and nickel, as well as a large proportion of iron and silica. Gold, silver, and copper are not eluted from carbon with hot or cold acid. Coating of the surface of the carbon with calcium carbonate could result

in reduced gold-adsorption efficiency. The calcium carbonate is probably derived partially from the catalytic oxidation of free cyanide in the contacting circuit, with the formation of ammonia and carbon dioxide:



Davidson and Tumilty⁷ report that acid washing of spent carbons prior to thermal regeneration has the following important additional functions.

- (a) As calcium, magnesium, and iron are known catalytic oxidants for the steam-carbon gasification reaction, acid washing of the carbon prior to thermal regeneration will minimize carbon losses and maintain the physical hardness of the carbon. Thermogravimetric analyses indicated that the oxidative loss in mass of carbons increased in the following sequence: virgin carbon (0,5 kg Ca/t) < eluted carbon washed with hot acid (1,2 kg Ca/t) < eluted carbon washed with cold acid (5,4 kg Ca/t) < eluted carbon not washed with acid (23 kg Ca/t). The use of higher reaction temperatures and longer residence times may result in more efficient regeneration of the carbon following acid washing.
- (b) The partial removal of silica accomplished by washing with hot acid, followed by elution of the gold, will prevent, to some extent, the formation of refractory crystalline or sintered silicates on the carbon surface during regeneration. Severe silicate fouling of carbon has been reported in several CIP operations, where the activity of the fouled carbon was restored only by treatment with hydrofluoric acid.
- (c) Acid washing of carbon is a recognized form of chemical regeneration, in many instances, that may well diminish the frequency of the need for thermal regeneration. Davidson and Tumilty⁷ report that carefully monitored CIP pilot operations at AARL indicated that non-regenerated carbon can be re-used some 5 or 6 times with little fall-off in activity when a wash with hot acid (93 °C) is used prior to the AARL solution.
- (d) Acid washing of the carbon after elution of the gold is not advisable, since the furnace may be severely corroded by the chlorides.

Influence of Temperature and Residence Time

The influence of temperature and residence time on the selective oxidation of pyrolysed residues was described earlier, e.g. in equations (7) to (10). Within strict limits (approximately 650 to 900°C), a trade-off of temperature against residence time can yield optimum thermal reactivation of spent carbon. However, at temperatures above about 950°C, even very short residence times are likely to lead to excessive losses of activated carbon. On the other hand, at temperatures below 650°C, the rate of steam-carbon gasification becomes negligible, and impractically long residence times may be needed for the proper reactivation of carbon.

Structural Changes during Thermal Treatment of New Carbon

In order to understand the various intraparticle structural changes that occur during progressive thermal treatment of an activated carbon, Van Vliet and Venter²⁵ tested a new activated carbon based on bituminous coal under a range of regeneration conditions. The various sequential reactions typical of the thermal treatment of porous activated carbon are illustrated in Fig. 4 for a peak furnace temperature of 950 °C. The first 10 minutes of treatment yielded small increases in the volume of the micropores and macropores, possibly owing to the removal of small amounts of substances adsorbed during transport and storage, and/or further refinement in the degree of activation of the raw material. During the residence-time interval from 10 to 30 minutes, an almost stoichiometric conversion of the micropores to mesopores took place, but the macropores were largely unaffected. The slight increase in the total pore volume during this period was probably due to erosion of the matrix between the micropores. After 30 minutes, further conversion of the micropores to larger pore types occurred, as well as progressive destruction of the activated-carbon matrix to yield additional large-pore volume. The net result was an extensive loss of micropore volume, an increase in mesopore and macropore volume, and a concomitant decrease in mechanical strength.

Conclusions based on total pore volume alone would therefore be very misleading since the total pore volume reflects only the net effect of substantial intraparticle changes. The micropore volume decreased by 44 per cent during the total 60-minute residence time, and the mesopore and macropore volumes increased by 66 and 50 per cent respectively. This has important practical implica-

tions, particularly for operation during the residence-time interval from 10 to 30 minutes, as indicated for particle density, apparent density, and iodine number in Fig. 4. These properties do not change much here, and neither does the total pore volume, yet the micropores are rapidly being converted to mesopores. In this instance, the desired 'end point' (i.e. at a residence time of 10 minutes) is not sensitive to the routinely monitored apparent density (or particle density) and iodine number, and so the on-line monitoring of an additional quality index is desirable.

Fig. 5 depicts the pore-volume distributions for the thermal treatment of new carbon at a peak furnace temperature of between 700 and 950 °C and 0 (new) to 60 minutes of residence time. Each of the graphs for the volume of the micropores and the mesopores plus macropores in the particles represents an experimental matrix of six temperatures by thirteen residence times, with additional smooth interpolation lines between data lines to facilitate three-dimensional representation. A plateau region of operating conditions (700 to 850 °C peak furnace temperature for 0 to 20 minutes) is evident where negligible damage occurs to the intraparticle structure. Above 850 °C and 20 minutes of residence time, structural damage occurs largely by the conversion of smaller pore types to larger ones. The resultant carbon is very soft and fragile.

Structural Changes during Regeneration of Spent Carbon from Water Renovation

Fig. 6 presents the pre-size distributions from a parametric study of temperature and residence time for the regeneration of spent carbon. As before, activated carbon based on bituminous coal was used but, in this case, it had been saturated during water-renovation operations.

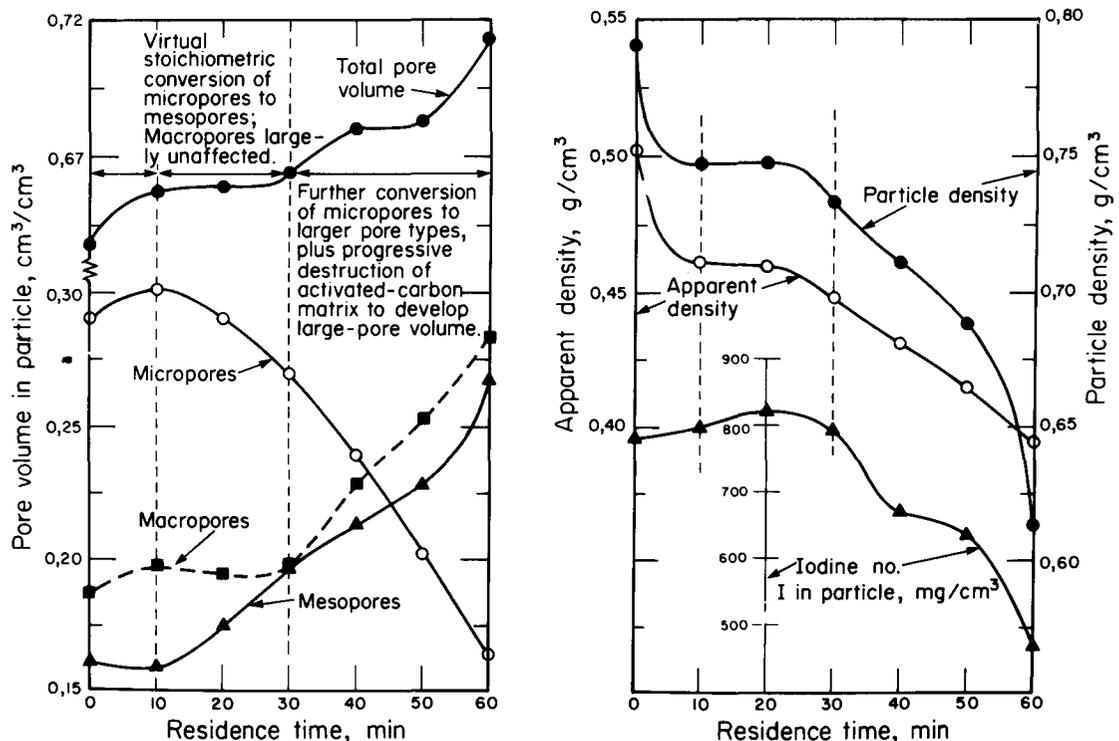


Fig. 4—Thermal treatment of new carbon at 950 °C under steam; stages of intraparticle structural change (after Van Vliet and Venter²⁵)

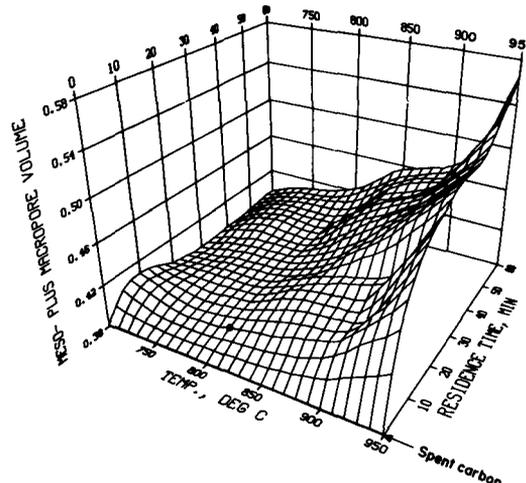
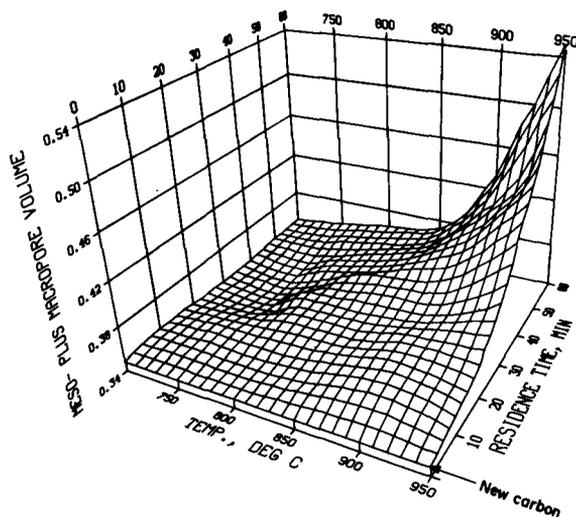
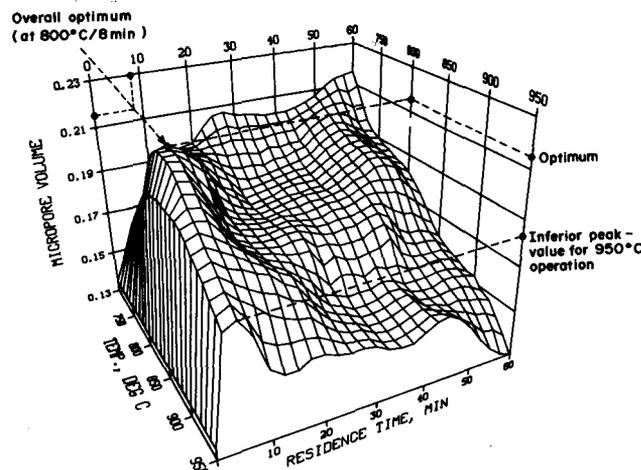
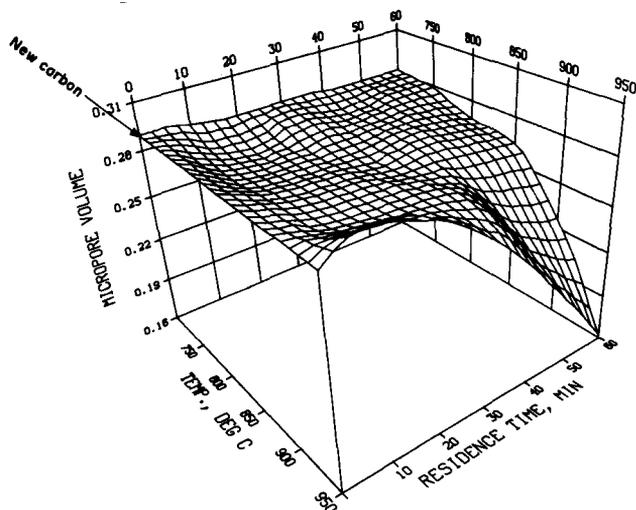


Fig. 5—Thermal treatment of new carbon under steam: effects of temperature and residence time on the volume of the micropores and of the mesopores plus macropores in the particles (after Van Vliet and Venter²⁵)

Fig. 6.—Regeneration under steam of spent carbon from water renovation: effect of temperature and residence time on the volume of the micropores and of the mesopores plus macropores in the particles (after Van Vliet and Venter²⁵)

During the first few minutes of regeneration, congested micropore volume was substantially restored. The recovery of micropore volume was at a maximum after 8 minutes of residence time and at a peak furnace temperature of 800°C. Equivalent levels of intraparticle structural restoration were achieved at, for example, 800°C and 10 minutes or 700°C and 60 minutes. However, it was not possible to even approach the overall optimum degree of micropore restoration for any residence time at 950°C, since that temperature effected regeneration conditions that were too intense.

At high temperature and prolonged residence time (e.g. 960°C and 60 minutes), there was excessive loss of micropore volume and an increase in mesopore and macropore volume (according to the mechanisms described earlier), and the resultant carbon particles were very fragile.

References

1. COONEY, D.O., NAGERL, A., and HINES, A.L. Solvent regeneration of activated carbon. *Wat. Res.*, vol. 17, no. 4. 1983. pp. 403-410.
2. CROSS, W.H., and SUIDAN, M.T. Organic solvent regeneration of granular activated carbon. *Report PB 83-150201 NTIS Environmental Resources Center, Georgia Institute of Technology, Atlanta, 1982.*
3. ROLLER, M.A., SUIDAN, M.T., CROSS, W.H., and VARGO, S.A. Regeneration of five carbons with methanol. *J. Environmental Eng. Div., Proc. Am. Soc. Civ. Eng.*, vol. 108 (EE6). 1982. pp. 1361-1377.
4. PICT, R.D., DILLMAN, T.R., BOURKE, D.J., and DEFILIPPI, R.P. Regeneration of adsorbents by a supercritical fluid. *AIChE Symp. Ser.*, no. 78 (219). 1982. pp. 136-149.
5. SLAVINSKII, A.S., VELIKAYA, L.P., and KARIMOVA, A.M. Electrochemical regeneration of activated carbon saturated with p-nitroloene. *Khim. Teknol. Vody*, vol. 6, no. 6. 1984. pp. 509-511.
6. VAN VLIET, B.M. Comparative efficacy of extractive and thermal regeneration of activated carbon. *Proceedings of the 14th IWSA International Congress, Zürich, 6-10 September 1982.*

7. DAVIDSON, R.J., and TUMILITY, J.A. *A review of the AARL process for the elution of gold from activated carbon*. Anglo American Research Laboratories, Crown Mines, 1985.
8. JONES, J.L., and GWINN, J.E. Activated carbon regeneration apparatus. *Environmental Prog.*, vol. 2, no. 4. 1983. pp. 226-235.
9. VON DREUSCHE, C. Regeneration systems. *Activated carbon adsorption for wastewater treatment*. Perrich, J.R. (ed.). Boca Raton (USA), CRC Press, 1981.
10. URANO, K., YAMAMOTO, E., and TAKEDA, H. Regeneration rates of granular activated carbons containing adsorbed organic matter. *Ind. Eng. Chem., Process Des. Dev.*, vol. 21, no. 1. 1982. pp. 180-185.
11. SUZUKI, M., MISIC, D.M., KOYAMA, O., and KAWAZOE, K. Study of thermal regeneration of spent activated carbon: Thermogravimetric measurement of various single component organics loaded on activated carbons. *Chem. Eng. Sci.*, vol. 33. 1978. pp. 271-279.
12. PEARL, I.A. *The chemistry of lignin*. New York, Marcel Dekker, 1967.
13. VENNEKENS, M.J.A., and VAN VLIET, B.M. Thermal analytic study of the influence of oxidative water pretreatment on adsorbate characteristics in spent activated carbon. *Wat. S.A.*, vol. 11, no. 3. 1985. pp. 111-120.
14. UMEHARA, T., HARRIOT, P., and SMITH, J.M. Regeneration of activated carbon. Part 2. Gasification kinetics with steam. *AIChE J.*, vol. 29, no. 4. 1983. pp. 737-741.
15. WALKER, P.L., JR., RUSINKO, F., and AUSTIN, L.G. Gas reactions of carbon. *Adv. in Cat.*, vol. 11. 1959. pp. 133.
16. CHIHARA, K., SMITH, J.M., and SUZUKI, M. Regeneration of powdered activated carbon. Part 1. Thermal decomposition kinetics. *AIChE J.*, vol. 27, no. 2, 1981. pp. 213-220.
17. KLEI, H.E., SAHAGIAN, J., and SUNDSTOM, D.W. Kinetics of the activated carbon-steam reaction. *Ind. Eng. Chem., Process Des. Dev.*, vol. 14, no. 4. 1975. pp. 470-473.
18. MCKEE, D.W. The catalysed gasification of carbon. *Chem. Phys. Carbon*, vol. 16, no. 1. 1981.
19. SMISEK, M., and CERNY, S. *Active carbon*. New York, American Elsevier Publishing Co., 1970.
20. JUHOLA, A.J. Regeneration of activated carbon. Conference on Activated Carbon in Water, University of Reading, 3-5 April, 1973.
21. HARRIOT, P., and CHENG, A.T. Kinetics of spent activated carbon regeneration. *AIChE J.*, vol. 34, no. 10. 1988. pp. 1656-1662.
22. PRODAN, L.N., KOGANOVSKII, A.M., and KOFANOV, V.I. Catalytic regeneration of active carbon saturated with SAS, DYE and phenol. *Khim. Tekhnol. Vody*, vol. 10, no. 3. 1988. pp. 278-280.
23. PRODAN, L.N., KOFANOV, V.I., and KOGANOVSKII, A.M. Conditions of catalytic oxidation of hydrocarbons in waste gases during low-temperature regeneration of active carbon after waste water treatment. *Khim. Tekhnol. Vody*, vol. 9, no. 4. 1987. pp. 313-316.
24. MAMONTOVA, A.A., KOFANOV, V.I., and KLIMENKO, N.A. Modification of active carbon for its catalytic regeneration. *Sov. J. Wat. Chem. Technol.*, vol. 9, no. 1. 1987. pp. 105-107.
25. VAN VLIET, B.M., and VENTER, L. Infrared thermal regeneration of spent activated carbon from water reclamation. *Wat. Sci. Technol.*, vol. 17. 1985. pp. 1029-1042.

Bill Venter Prestige Lecture

This year's Bill Venter Prestige Lecture was presented by Dr Horst Wagner, Senior General Manager Operations, Chamber of Mines, and a Past President of The South African Institute of Mining and Metallurgy. The lecture had as its theme the role of technology in a developing South Africa from a mining perspective, and emphasized the international role of South Africa's mining industry and its sensitivity to the prices of commodities and to inflation.

The Bill Venter Prestige Lecture is sponsored each year by Dr Bill Venter, Executive Chairman of Altron, and is presented by the Council and Rectorate of the Technikon Witwatersrand.

Dr Wagner also examined economic developments in the gold- and coal-mining industries, and stressed the importance of linking wage increases to improved productivity by saying, 'It has been shown that the present dif-

ficulties of the gold-mining industry are largely linked to huge increases in the wage bill without increases in labour productivity and a decrease in the grade of ore mined. Wage increases on the coal mines have been accompanied by significant improvements in labour productivity. These were achieved through mechanization and the introduction of new methods of mining.'

The lecture went into some detail about the reasons for the gold-mining industry's lack of success in developing and applying suitable technology to improve productivity. Of these, he considered the most important to be the difficult environmental conditions in South African gold mines and a lack of technically skilled and trained manpower.

This critical shortage of manpower, he said, points to a need for a national strategy to ensure an adequate supply of technically qualified personnel.

New Council member of SABS

Mr B.C. Alberts was appointed member of the SABS Council on 1st November, 1990. He is Senior General Manager, Mining, of Iscor.

Mr Alberts was born in Pretoria in 1939 and obtained the B Eng (Agric) degree, as well as the B Eng (Mining) degree, from the University of Pretoria. He also acquired the Mine Manager's Certificate of Competency for Metalliferous and Fiery Mines. In addition, he is a registered professional engineer.

In business, he is a director of seven companies which

are, *inter alia*, active in the mining of tin, zinc, and coal, and in shipping. Mr Alberts served on various boards, including the Council of The SA Institute of Mining and Metallurgy of which he was President, the Pretoria University Board, the National Advisory Council for Geological Sciences, the Afrikaanse Handelsinstituut and the Coal Committee of the National Energy Board.

An ardent rugby player, he played for Tukkies and northern Transvaal, the SA Universities, SA Barbarians, and the SA Gazelle team that visited Argentina.