

# A pre-burial adsorption model for the genesis of gold in the Witwatersrand

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## SYNOPSIS

The chemistry related to the adsorption of gold, uranium, and transition-metal ions onto algal biomass (activated carbon) is related to the genesis of the Witwatersrand.

Detrital gold being washed into the early basin, together with cyanide generated in the atmosphere, would have solubilized as the stable aurocyanide complex, the necessary oxygen being produced from the photosynthesis of carbon dioxide by primitive algae. Pebble-type conglomerates, while providing for the free movement of solutions containing the vital nutrients for prolific algal growth, would have screened off the sunlight, which would otherwise have degraded any free cyanide in solution. With the subsequent decomposition of the algal deposits, it is surmised that carbon-rich layers having adsorptive properties similar to those of activated carbon formed in the conglomerates. Under these conditions, gold (silver) in solution would have been adsorbed selectively as the cyanide complex, together with uranium as the carbonate complex. Any transition-metal ions present would also have been adsorbed onto such a substrate.

The subsequent burial and compression of the gold-rich conglomerate with temperatures rising to about 400°C would then have reduced the adsorbed gold to the metal in a single segregated gold-silver metal phase (95 to 99 per cent of the contained gold), while leaving behind a sulphide phase rich in iron, base metals, and arsenic and containing some gold and silver. The recrystallization of this latter phase may explain the presence of the rather consistent contents of secondary pyrite in the Witwatersrand conglomerates. Similarly, uranium minerals, some rich in titanium and carbon, may also have formed.

An adsorption model would explain the very consistent trends in the gold-to-silver ratios of individual reefs in the Witwatersrand, which suggest an extensive hydrothermal system approaching isothermal equilibrium. Also, as gold grades increase, so silver grades generally decrease, indicating the sequential displacement of silver by gold as classically obtained with activated carbon.

## SAMEVATTING

Die chemie verbonde aan die adsorpsie van goud, uraan en oorgangsmetaalione op 'n algale biomassa (geaktiveerde koolstof) hou verband met die oorsprong van die Witwatersrand.

Detritale goud wat in die vroeë kom ingespoel is, het saam met sianied wat in die atmosfeer gegenerereer is, oplosbaar geraak as die stabiele auroasianiedkompleks. Die nodige suurstof is verskaf deur die fotosintese van koolstofdioksied deur primitiewe alge. Spoelklipagtige konglomerate wat vir die vrye beweging van oplossings met die lewensbelangrike voedingstowwe vir die weelderige groei van alge gesorg het, het die sonlig afgekeer wat andersins enige vry opgeloste sianied gedegradereer het. Met die daaropvolgende ontbinding van die algafsettings het daar vermoedelik koolstofryke lae met adsorpsie-eienskappe soortgelyk aan dié van geaktiveerde koolstof in die konglomerate gevorm. Onder hierdie omstandighede sou opgeloste goud (silwer) selektief as die sianiedkompleks, saam met uraan as die karbonaatkompleks geadsorbeer word. Enige aanwesige oorgangsmetaalione sou ook op so 'n substratum geadsorbeer word.

Die daaropvolgende begraving en saampersing van die goudryke konglomeraat met temperature wat tot ongeveer 400 °C gestyg het, sou dan die geadsorbeerde goud tot die metaal gereduseer het in 'n enkele gesegregeerde goud-silwermetaalfase (95 tot 99 persent van die ingeslote goud), terwyl dit 'n sulfiedfase ryk aan yster, onedelmetale en arseen agtergelaat het wat ook 'n bietjie goud en silwer bevat het. Die herkristallisering van laasgenoemde fase kan moontlik die aanwesigheid van 'n taamlik konstante sekondêre pirietinhoud in die Witwatersrandse konglomerate verklaar. Uraanminerale, waarvan sommige ryk aan titaan en koolstof is, kan ook op dieselfde wyse gevorm gewees het.

'n Adsorpsiemodel sal die uiters konstante tendense in die goud-silwer verhouding van individuele riewe van die Witwatersrand verklaar wat dui op 'n uitgebreide hidrotermiese stelsel wat na aan isotermsiese ewewig kom. Die silwergrade wat oor die algemeen afneem namate die goudgrade toeneem, dui ook op die sekwen্সiale verplasing van silwer deur goud wat algemeen met geaktiveerde koolstof verkry word.

## Introduction

Recent studies<sup>1</sup> on the genesis of the gold in the Witwatersrand tend to indicate that hydrothermal fluids have affected a large part of the basin and, as such, raise serious questions concerning the current placer model<sup>2</sup>. The predictive capacity of the placer model is questioned here, and an alternative chemical viewpoint is presented that emphasizes the possible role played by activated carbon in the genesis of the Witwatersrand.

A rather incongruous relationship between the noble

metal gold and the common element carbon is often apparent in many gold-bearing orebodies. Not only are gold and carbon very often found together in the same stratigraphical horizon in nature—perhaps indicating some sort of genetic relationship—but activated carbon is well known as a very selective adsorbant for gold and is widely used in many extraction circuits. Questions must therefore be asked as to whether the chemistry involved in the extraction of gold by activated carbon bears any relationship to the genesis of the gold in the Witwatersrand. The present paper is a preliminary attempt to answer some of these questions.

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### Activated Carbon

In many ways activated carbon is a unique material with properties not possessed by any other class of organic substance. Since activated carbon usually contains considerable quantities of adsorbed oxygen and hydrogen, the term *carbon* is perhaps a misnomer. It is essential to regard activated carbon as a complex organic polymer, and not merely as an amorphous form of the element carbon. Activated carbon, however, differs from other organic polymers in having an exceptionally large surface area and in being a good conductor of electricity. Many of its intriguing characteristics stem from the latter fact, as well as being related to the various functional groups present on the carbon surface. A better understanding of both the complex physical and chemical characteristics of activated carbon is thus a prerequisite to an understanding of the factors influencing gold adsorption and to the formulation of any adsorption mechanism.

Activated carbon can be made by the heating of virtually any carbonaceous material in a mildly oxidizing atmosphere. The physical and chemical properties of the activated carbon are influenced to a large degree by both the nature of the source material and the conditions of activation. During the course of activation, the carbon develops a porous graphitic structure of molecular dimensions with an extraordinarily large internal surface area on which adsorption can take place. The quantity, size, and shape of these pores distinguish both the various types of activated carbons and their subsequent application. In general, raw materials with a dense, cellular structure produce a hard, brittle product, and it is for this reason that carbons made from coconut shell are used almost exclusively in the gold-mining industry.

Activated carbons are, however, also produced in nature<sup>3</sup>; many peats, brown coals, and even decomposed vegetation display similar adsorptive properties, particularly with regard to the selective adsorption of gold. In particular, algal biomass<sup>4</sup> has been shown to be a binding medium for transition metals, as well as for gold. Moreover, gold is efficiently and reversibly bound to the algal biomass from gold solutions of as low as  $10^{-9}$  M. The ligating atom in the biomass appears to be sulphur.

### Adsorption of Gold

The selective adsorption of metal-cyanide complexes onto activated carbon appears to be related to the solubility and charge of the ion-paired adsorbed species. While the less soluble monovalent dicyano complexes of gold, silver, and copper have all been shown to be strongly adsorbed by carbon, the more soluble divalent and trivalent tri- and tetracyano complexes (e.g. copper, nickel, and zinc) are only weakly adsorbed, while the very soluble hexa- and octacyano complexes (e.g. cobalt and iron) are not adsorbed to any marked degree.

Under plant conditions, the selective adsorption of gold onto activated carbon is thought to be related to the solubility of the ion-paired species  $\text{Ca}^{2+} [\text{Au}(\text{CN})_2]_2^-$ . Conditions favouring gold adsorption include low temperature, low cyanide concentrations, low alkalinity, and the presence of an adsorption medium of high ionic strength containing  $\text{Ca}^{2+}$  ions. Also, the concentration of free cyanide has a significant effect on the selectivity of carbon for gold from typical plant solutions or pulps.

Under plant conditions, activated carbon is most selective in adsorbing gold from such complex mixtures. Selective metal adsorption appears to take the form of a complex displacement sequence, gold followed by silver being the most strongly adsorbed metal species. No well-defined sequence of metal displacement can be formulated since the adsorption of these metal values is sensitive to such processing parameters as pH, free cyanide concentration, temperature and, of course, the relative concentration of the metal values in a particular plant solution or pulp. In general, the selectivity of carbon for gold increases with an increase in pH or in free cyanide concentration.

### Adsorption of Uranium

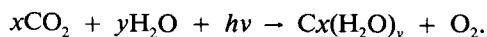
Attempts at the Anglo American Research Laboratories (AARL) to adsorb uranium onto activated carbon under oxidizing acid conditions have not been successful. However, activated carbon pretreated with titanium chloride or with zirconium chloride has been shown to be very efficient at scavenging uranium.

As the reduced  $\text{U}^{+4}$  carbonate complex of uranium is less soluble than the  $\text{U}^{+6}$  complex, the adsorption of uranium onto activated carbon under alkaline conditions as the carbonate complex can be expected to be more efficient. (A large commercial plant in Japan is using titanium-impregnated carbon to recover uranium from sea water.)

### Proposed Model

It seems likely that solar ultraviolet light and lightning were the main sources of energy to affect the chemistry of the early atmosphere<sup>5</sup>. In Miller's classic experiments (1953), in which mixtures of  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$  were subjected to electrical discharges, substantial quantities of organic polymers and amino acids, together with large amounts of cyanide and aldehydes, were formed. The organic chemistry of the early oceans was thus probably most complex. Organic compounds including cyanide were almost certainly generated in the atmosphere and carried into the oceans.

In the case of the Witwatersrand inland sea, it is thus probable that gold in the form of the very stable  $\text{Au}(\text{CN})_2^-$  complex ( $k = 10^{-38}$ ) tended to concentrate in solution. Any detrital gold being washed into this environment may thus have been solubilized, the necessary oxidant being produced from the photosynthesis of  $\text{CO}_2$  by the living algae:



Thus, while the early atmosphere may have been mildly reducing and deficient in oxygen, the Witwatersrand basin may well have been saturated with oxygen via this reaction.

It should be noted that  $\text{Au}(\text{CN})_2^-$  is stable towards high doses of ultraviolet light and ozone, while  $\text{Ag}(\text{CN})_2^-$  ( $k = 10^{-22}$ ) becomes partially decomposed.

Hydrothermal springs from faults along the edge of the basin<sup>6</sup> could have been an additional source of gold.

In regard to the free movement of solutions through an original sedimentary geological formation, only rudites such as a pebble type of conglomerate would afford such free flow. The presence of solutions containing vital

nutrients for the proliferation of primitive algal growth (e.g. potassium and ammonia) may explain the very wide extent of such algal growth in the Witwatersrand conglomerates some 3000 million years ago. Little evidence for such algal growth is present in the quartzites and sandstones. Furthermore, a pebble type of formation would have screened off sunlight, which would otherwise have degraded any cyanide in solution.

With the subsequent decomposition of such algal deposits under what were thought to be mildly oxidizing conditions, a deposit of active biomass displaying adsorptive properties may have formed. Under these conditions, gold (silver) in solution as the cyanide complex would have been selectively adsorbed onto this active substrate.

Furthermore, the active substrate, in which the ligating atom appears to be sulphur, would also have scavenged the iron and base metals present in very dilute solution. Uranium present as the carbonate complex may also have been adsorbed onto the carbon-rich biomass.

The subsequent burial and compression of the gold-rich conglomerate with temperatures rising to about 400 °C would then have reduced the adsorbed gold to the metal as a single gold-silver metal phase (95 to 99 per cent of the contained gold), leaving behind a sulphur-rich phase containing iron, base metals, and arsenic<sup>7</sup> with some gold and silver. The recrystallization of this latter phase may explain the presence of the rather consistent secondary pyrite found in the Witwatersrand conglomerates, and may also explain the sulphurization of the heavy ferruginous minerals as proposed by Ramdohr<sup>8</sup>. Similarly, uranium minerals, some rich in titanium and carbon, may also have formed.

#### Gold-to-Silver Ratios

The most consistent trends in the gold-to-silver ratios of individual reefs in the Witwatersrand basin are explained satisfactorily only in terms of an extensive hydrothermal system approaching isothermal equilibrium. In a major analytical survey<sup>9</sup> of the economic reefs being mined in the Anglo American Group, a near-perfect linear relationship was obtained in all instances for gold grades plotted against total precious-metal values (gold + silver) (Table I). As an example, the values obtained from the Leader Reef in the Welkom area are presented in Fig. 1. This graph also shows that, in all the reefs considered, as the gold grades increased, so also did the gold-to-silver ratio, as illustrated in Fig. 2. The sequential displacement of silver by gold as classically obtained using activated carbon is strongly suggested.

While it would appear that 90 to 95 per cent of the contained gold in the Witwatersrand reefs is present as 20 to 50 µm electrum particles with gold-to-silver ratios approaching 10 in the case of the higher-grade reefs, a small proportion (1 to 2 per cent) of the gold is associated with the pyritic phases, together with relatively high base-metal and arsenic values. The gold-to-silver ratios in these phases are very different, falling in the region between 0,6 and 0,9. The low solubility of silver sulphide would explain the concentration of silver in these pyritic phases.

#### Particle Size

Both the small size and the very often irregular shapes of the particles of detrital gold found in the Witwaters-

TABLE I  
THE LINEAR RELATIONSHIP BETWEEN GOLD AND SILVER IN  
VARIOUS WITWATERSRAND REEFS

Reef	Plot of $Y(\text{Au g/t})^*$ $= a X(\text{Au g/t} + \text{Ag g/t})^\dagger + b$		
	<i>a</i>	<i>b</i>	Correlation coefficient
Western Holdings Leader Reef	0,906	-0,228	0,994
Vaal Reefs			
Elsburg Reef	0,909	-0,497	0,999
Ventersdorp Contact	0,899	-0,368	0,997
Vaal Reefs	0,912	-0,479	0,999
Western Deep Levels			
Ventersdorp Contact	0,929	-1,297	0,999
Carbon Leader	0,913	-0,658	0,999
Welkom			
Basal Reef	0,923	-0,540	0,999
Leader Reef	0,910	-0,360	0,999

\* Fire assay followed by parting

† Fire assay (gravimetric)

rand are difficult to explain according to a placer model. On the other hand, gold adsorbed onto activated carbon as the aurocyanide complex and subsequently heated to 400 °C, which would reduce the gold to the metal, may well resemble these particles of detrital gold. At ambient temperatures, activated carbon is not able to reduce gold to the metal when adsorbed as the aurocyanide since the reduction potential of  $\text{Au}(\text{CN})_2^-$  is -0,6 V (n.H.e) compared with 0,0 V for activated carbon<sup>10</sup>. However, on being heated to about 400 °C, the gold that had migrated to the surface of the carbon would have been reduced to the metal in small irregular-shaped particles. A gold-silver mixture adsorbed onto activated carbon as the respective cyanide complexes in the ratio 10 Au : 1 Ag has been observed to respond in a similar way. It was also observed that the particle size of the reduced gold was very dependent on the particle size of the carbon used. (Synthetic ore aimed at simulating a milled reef is prepared at AARL using loaded activated carbon that is calcined subsequently to remove the carbon.)

#### Chemical Associations

Gold occurs in two important end-member chemical associations in the Witwatersrand<sup>2</sup>: the first, corresponding to between 95 and 99 per cent of the contained gold, is present as discrete particles of electrum and is characterized by Au-C in carbon-rich seams or layers, and the second is Au-Fe-S-As, being characterized by pyrite-bearing conglomerates. Similarly, uranium has two important associations: U-Ti in the conglomerates, and U-C in the carbon-rich seams. These chemical associations are found in reefs throughout the basin, but they are not mutually exclusive and are rarely discrete.

#### Dilute Solutions

Activated carbon is currently used to scavenge gold efficiently from dam return circuits with a gold concentration of only 20 ng/t ( $10^{-9}$ ), where loading on the

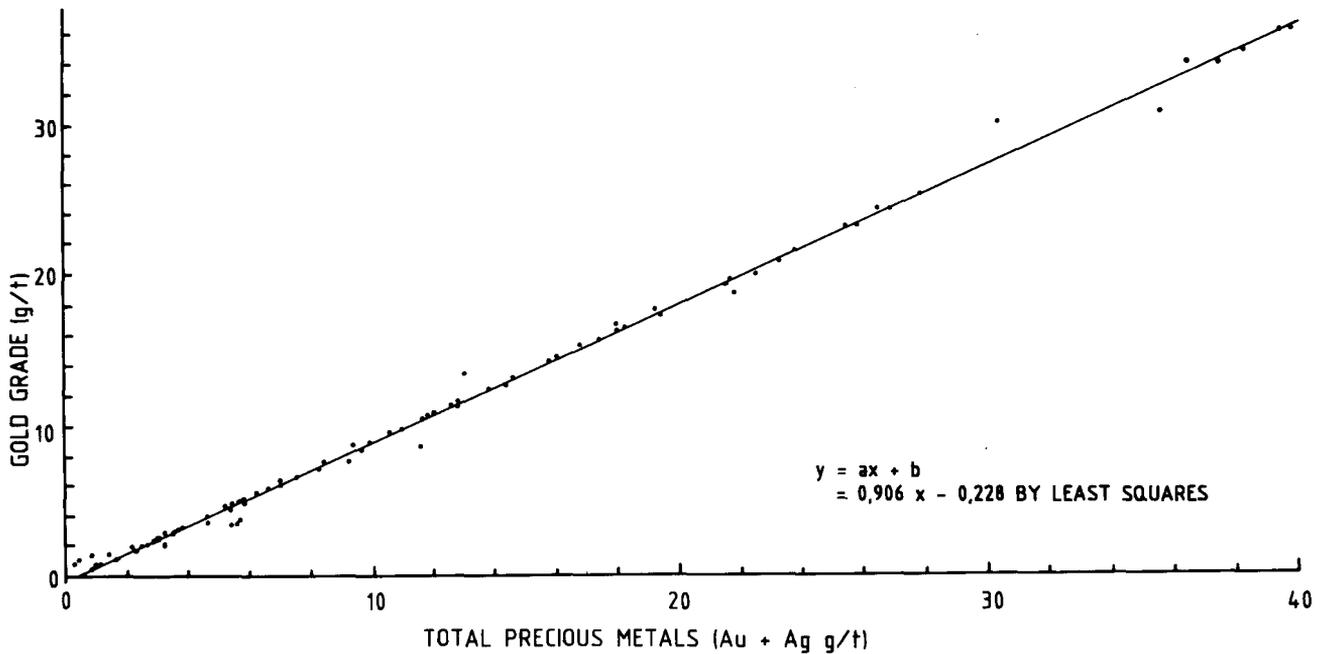


Fig. 1—The linear relationship between the gold and silver values found in the Welkom Leader Reef

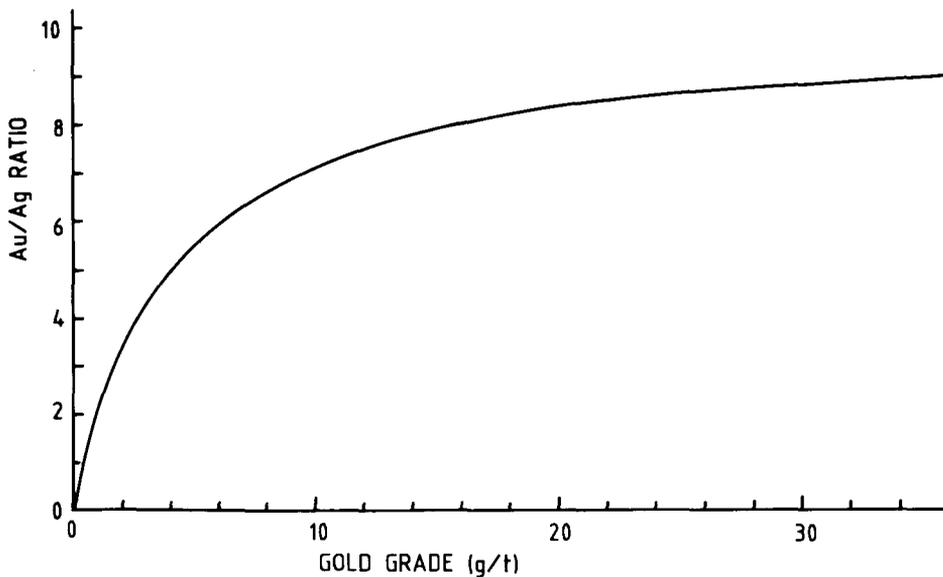


Fig. 2—The increase in gold-to-silver ratio with gold grade in the Welkom Leader Reef, illustrating the sequential displacement of silver by gold

carbon has approached  $\times 50\,000$ , i.e. giving a gold loading on the carbon of 1 kg/t. The concentration of gold in sea water is estimated to be 5 pg/t ( $10^{-12}$ ). Also, algal biomass<sup>4</sup> has been shown to efficiently and reversibly adsorb gold present as  $\text{Au}(\text{CN})_2^-$  at concentrations as low as  $10^{-9}$  M.

#### Carbon Deposition and Decomposition

Any decaying algal deposit would have become sedimented to the bottom of the conglomerate prior to burial, with the pebbles acting as a trap for any such material. Subsequent decomposition (and activation) of the biomass with carbon being lost as carbon dioxide to the atmosphere was most likely. (Activated carbon is a most effective scavenger for oxygen.) With this decomposition,

high residual potassium and aluminium values would have occurred, which may explain the presence of the phyllosilicates found as cementing material in the conglomerates. Following adsorption, high gold values, particularly towards the footwall of the reef, may also have occurred.

#### Other Lixiviants

While the proposed adsorption model would suggest that gold is adsorbed as an aurocyanide complex, other possible lixiviants should also be considered.

(1) For gold dissolved as the  $\text{AuCl}_4^-$  complex, an acidic chloride medium is required. This complex is strongly adsorbed onto activated carbon. Having a reduction

potential  $E^\circ = 1,0 \text{ V}$ , it is reduced directly to the metal by activated carbon ( $E^\circ = 0,0 \text{ V}$ ). However, the silver complex  $\text{AgCl}_2^-$  ( $E^\circ = 0,2 \text{ V}$ ) is soluble only in the presence of excessive salt concentrations (200 to 300 g of NaCl per litre) and, even if silver had been adsorbed onto carbon, its sequential displacement by gold would not have been possible because of the direct reduction of both the gold and the silver to their respective metals. No adsorption of sulphide ions would occur in an acidic chloride medium because of the instability of sulphide ions in such a medium.

- (2) Gold forms a very soluble sulphide,  $\text{AuS}^-$ , which is stable under alkaline conditions but which is not adsorbed onto activated carbon. However, silver sulphide is very insoluble and, if adsorbed onto carbon, is difficult to elute. The selective adsorption of gold and silver onto activated carbon as sulphides would thus appear to have been impossible.
- (3) While gold and silver are both soluble in ammoniacal solution as their thiosulphate complexes, little information on the adsorption of these complexes onto activated carbon is currently available. Alkaline sodium thiosulphate at ambient temperature is an excellent eluant for silver adsorbed onto carbon as the cyanide complex<sup>11</sup>, suggesting that the silver-thiosulphate complex is not adsorbed by activated carbon.

#### Discussion

The present preliminary investigation is an attempt by an extraction metallurgist to relate the chemistry of gold extraction by activated carbon to that of the mineralogy of the Witwatersrand—a subject with which the author

is not familiar. Nevertheless, while certain hydrothermal models for the Witwatersrand appear to be gaining some credibility, they are limited to post-burial effects. The present adsorption model suggests that pre-burial effects should also be recognized. Both the extent and the uniformity of the gold-bearing conglomerates in the Witwatersrand, together with the very consistent gold-silver values found, tend to support such a model.

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## Jet cutting

BHRA, The Fluid Engineering Centre, has released the final details of its Tenth International Symposium on Jet Cutting Technology.

The organizers have selected the Sonesta Hotel in Amsterdam, Holland, as a suitable venue for this meeting. The Symposium will be held in the Sonesta from 30th October to 2nd November, 1990, a fortnight earlier than originally scheduled.

Jetting techniques are now extensively employed for a wide range of tasks—from cutting difficult materials in hazardous environments to dismantling reactor vessels, as well as solving many cleaning and descaling problems. Today, the jetting industry is working to improve the profitability and efficiency of its systems in order to

extend the variety of applications of this valuable cold-cutting technique. This meeting will enable researchers, systems manufacturers, contractors, and end users to discuss current practice as well as explore opportunities for the future.

Further details can be obtained from  
 The Tenth Jet Cutting Symposium Organizer  
 BHRA, The Fluid Engineering Centre  
 Cranfield  
 Bedford MK43 0AJ  
 England.  
 Telephone (0234) 750422  
 Telex 825059  
 Fax (0234) 750074.