The adsorption of gold from cyanide solutions onto constituents of the reef, and its role in reducing the efficiency of the gold-recovery process

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SYNOPSIS

Evidence for the adsorption or re-precipitation of gold from cyanide solutions onto gangue minerals of the Witwatersrand reefs has been gathered over a number of years by various investigators. The evidence from tests using radioactive tracers is conclusive and indicates that adsorption contributes about 0,1 g/t to the total gold loss from conventional reduction works. The loss is a function of the alkalinity and cyanide concentration of the solution, and it appears to be affected by the extent of time between milling and cyanidation. The heavy minerals appear to be the strongest adsorbers, and the clay minerals somewhat less strong adsorbers. A sensitive qualitative test based on thin-layer chromatography permits the extent of adsorption and desorption to be readily determined.

SINOPSIS

Verskeie ondersoekers het oor 'n periode van jare bewyse gesoek vir die adsorpsie of herpresipitasie van goud uit sianiedoplossings op aarsteenminerale van die Witwatersrandse riwwe. Die bewyse van toetse met gebruik van radioaktiewe spoorders is afdoende en dui daarop dat adsorpsie ongeveer 0,1 g/t tot die totale goudverlies by konvensionele reduksiewerke bydra. Die verlies is 'n funksie van die alkaliniteit en sianiedkonsentrasie van die oplossing en word blykbaar beïnvloed deur die tydsverloop tussen die maal en sianiedisering. Die swaarminerale is blykbaar die sterkste adsorbeerders, terwyl die kleiminerale effens minder sterk adsorbeerders is. 'n Gevoelige kwalitatiewe toets wat op dunlaagchromatografie gebaseer is, maak dit moontlik om die mate van adsorpsie en desorpsie redelik maklik te bepaal.

INTRODUCTION

It is not generally recognized that the Witwatersrand reefs contain species that can cause re-precipitation of gold from the cyanide solutions normally employed. For instance, the latest text on gold metallurgy[1] notes that the various constituents of the pulp "may remove the cyanoaurate from solution" but does not discuss the topic. No reference to the adsorption of gold could be found in an earlier text[2]. However, in one of the earliest texts[3], some concern was expressed about the possibility of precipitation caused by carbon, iron, and other reducing constituents that are likely to be present. The authors noted that semi-burnt coal was frequently found in commercial lime and said: "Semi-burnt coal has been found capable, probably on account of its occluded hydrogen content, of precipitating gold to the extent of 3s. 7d. in value per lb. of coal"[4].

Naturally, however, the small amount of carbonaceous matter present in or introduced into mill pulps would be expected to have only a small effect. Such small effects could not be detected by classical methods of analysis. However, the availability of radiotracers in the early 1960's made it possible for the first time to quantify the magnitude of these effects. In this contribution, we wish to report the results of such studies that have been carried out over the past decade and that have not yet been published.

REVIEW OF EARLY WORK

In work carried out in the Union Corporation Group Research Laboratory in March 1963, in which ^{198}Au tracer was used in an attempt to determine the effectiveness of washing filter cakes, it was noted that the "dissolved gold content" of a filter cake tended to remain constant above a ratio of wash liquid to solid of 1:1. The magnitude of the effect varied from the pulp of one mine to that of another, but similar effects were noted in all the pulps. As all the gold that had entered the system had initially been in solution, it could be presumed that such an effect was due only to adsorption. These studies continued until at least mid-1964. On grounds of convenience, ^{110}Ag was introduced in place of ^{198}Au, and this tracer showed that adsorption occurred on a number of mill pulps. Carbon was shown not to be the prime adsorbing species, but adsorption on shale-like minerals appeared likely.

Virtually simultaneously with the initiation of studies by Union Corporation, Ltd, the Corner House Laboratories commenced a similar study of filtration using gold tracers. This work showed very definite adsorption when water was the wash solution, but, for the pulp tested, a 1:1 displacement followed by repulping, refiltration, and a second 1:1 displacement wash removed

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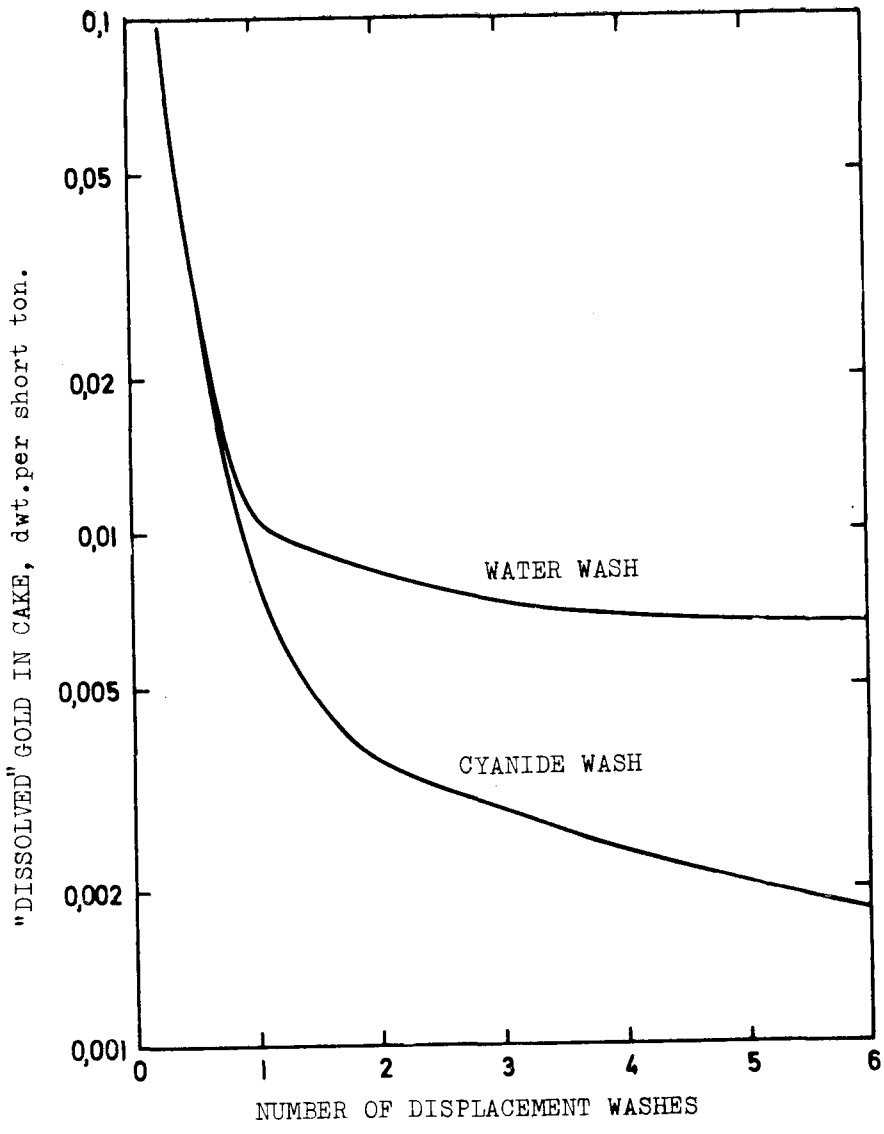

Fig. 1

significantly more adsorbed gold, provided the wash and repulp solutions contained 0,015 per cent NaCN and 0,010 per cent CaO. Typical results of this study are shown in Fig. 1. The general conclusions were identical to those reached by the Union Corporation: namely, that gold was not removed as easily from filter cakes as would be predicted by any theory based on mechanical entrainment of gold-bearing solution, and thus that gold must be adsorbed onto constituents of the reef.

In later work, the Corner House Laboratories attempted to study the effect of reverse leaching. In careful pilot-plant studies in which the washing procedure was closely controlled, it was found that, the higher the fineness of grind, the higher was the residue for a conventional leaching circuit, although the residue was lowered with increasing fineness of grind in a reverse leach. These results are indicated in Fig. 2. In this case it is possible that gold became more "coated" as the grinding proceeded, and that the coating was removed by reverse leaching. However, these results are also in agreement with a hypothesis based on adsorption, because finer grinding would lead to a larger area for adsorption and thus a greater degree of adsorption, whereas acid treatment might destroy the adsorptive properties of species present in the pulp.

In 1966, as a result of the findings outlined above, the Chamber of Mines Research Organization arranged for the Corner House Laboratories to investigate the adsorption of gold on constituents in the reef. In this paper, we review the findings of this investigation in detail.

INITIAL EXAMINATION OF THE FACTORS INFLUENCING ADSORPTION

The adsorption of gold on various natural clay minerals was studied by determination of the change in the concentration of radioactive gold in alkaline cyanide solutions after contact with the minerals. Corrections were found to be necessary for water absorption by the clay minerals. Kaolin, ball clay, fuller's earth, and bentonite showed essentially no adsorption of gold. "Wonderstone" (60-80 per cent pyrophyllite) showed marked adsorption at low cyanide and lime concentrations in solution. However, a sample of khaki shale from the Orange Free State, which was also high in pyrophyllite, showed no detectable adsorption under similar conditions, but various Basal Reef samples showed marked adsorption. The adsorption on one of these samples was studied under a variety of conditions. At very low cyanide and lime concentrations, the adsorption reaction was shown to be slow but reversible. At 5×10^{-7} per cent KOH, the amount of adsorption decreased as the cyanide concentration increased and as the initial gold concentration increased. At 5×10^{-6} per cent NaCN, the adsorption remained high as the alkalinity was increased, but dropped somewhat as the gold concentration increased. Under the conditions most closely approaching those on the plant (NaCN 5×10^{-2} per cent, KOH 5×10^{-7} per cent, and Au 8,6 g/t initially), the gold lost by adsorption was estimated to be about 1,6 g/t.

Because of the failure in the first studies to identify any clay minerals as being responsible for adsorption, attempts were made to identify other species that might be responsible. Uraninite and thucholite showed marked adsorption at low cyanide concentrations, irrespective of the concentration of gold in solution.

However, the adsorption largely disappeared at 0,03 per cent NaCN in solution. Coal was, however, shown to adsorb significant quantities of gold under all the conditions tested.

Some attempts to develop other techniques for the study of gold adsorption were made. For an ore sample that appeared to adsorb gold at low cyanide concentrations, no adsorption was observable at 0,02 per cent NaCN, even when the ore was split into a number of size fractions and each size fraction tested separately. An attempt to adsorb radioactive gold onto a polished section of reef and thus identify the locations of adsorption by autoradiography failed because radioactive-gold solution was retained in microcracks in the specimen. A pulse of radioactive gold was passed down a column containing the minus 75 plus 45 μm fraction of a typical pulp. Only about 60 per cent of the gold tracer was recovered by the time all evidence of radioactivity in the effluent from the column had disappeared. The solution used to wash the radioactivity down the column contained 0,1 per cent NaCN and 0,03 per cent CaO.

DETAILED STUDIES OF THE MORE IMPORTANT FACTORS

Very careful studies of the factors found in the initial examination to be important were then undertaken. The samples of minerals tested were ground to minus 20 μm and equilibrated with solutions containing radioactive gold for 20-30 h at a liquid-to-solid ratio of 4 or 8 to 1 by mass. All tests were done at least in duplicate, and the concentrations of cyanide, lime, and gold in the solution at equilibrium, and its pH, were determined. The following is a summary of the results.

(1) For reef samples from Harmony, the proportion of gold adsorbed decreased with time after milling but was still significant after 18 days; decreased with increasing cyanide concentration but was still significant in the presence of 0,055 per cent NaCN at equilibrium (initial NaCN concentration 0,4 per cent); and decreased with increasing gold concentration in solution.

(2) For gravity concentrates (about 75 per cent pyrite), the amount of adsorption also decreased with time after milling but remained significant after 18 days.

(3) For khaki shale, the amount of adsorption *increased* with time after milling but was significant 3 days after milling; decreased with increasing cyanide concentration but was significant in the presence of as much as 0,04 per cent NaCN at equilibrium; and was not significantly affected by the presence of large concentrations of gold in the solution.

(4) For thucholite, there was significant adsorption, even in the presence of as much as 0,13 per cent NaCN and 190 g of gold per tonne at equilibrium; and there was no significant difference in the adsorption observed at 6 or 18 days after milling.

(5) For quartz, the ratio of gold adsorbed (if any) to gold in solution was estimated to be below 0,03.

(6) For uraninite, there was no significant adsorption in the presence of about 0,020 per cent NaCN.

(7) For chalcopyrite, there was apparently no adsorption in the presence of as little as 0,003 per cent NaCN 3 days after grinding. However, strong adsorption was shown 18 days after grinding.

These results were considered in terms of various hypotheses to account for the effect of time after milling on the adsorption, and it was concluded that surface oxidation of the absorbing mineral species was the most probable cause, particularly as there was a correlation between cyanide consumption and time after milling for those species that showed a change in adsorption behaviour

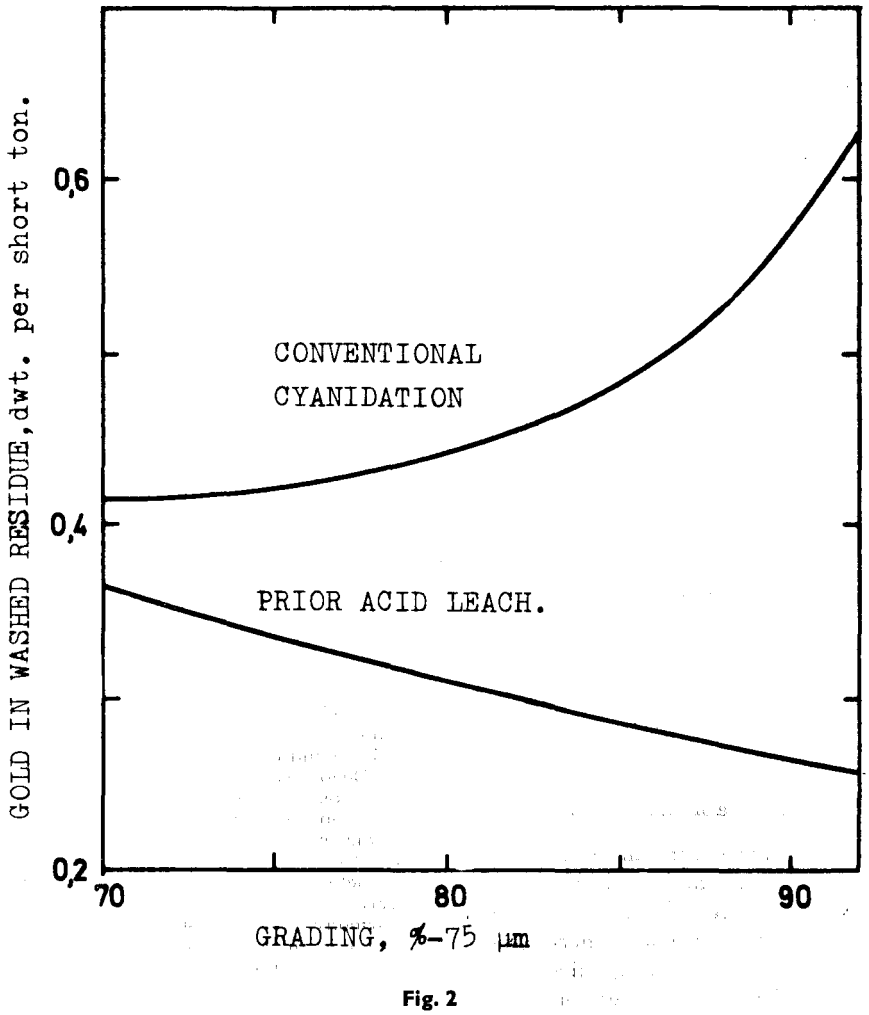

Fig. 2

with time. For a typical Orange Free State ore, the magnitude of the loss due to adsorption was estimated by summing the contributions of the various constituents. For equilibrium with solutions containing 8,5 g of gold per tonne and typical concentrations of cyanide and lime, the gold loss was estimated as being more than 0,20 g/t.

DETAILED TESTS ON SAMPLES FROM A SINGLE CIRCUIT

Repeated adsorption tests on various samples taken from the Harmony mill circuit were made. Four to six identical adsorptions were done on each sample under each set of conditions, and the results were compared statistically. Samples of the residue from a high-grade, reverse-leach gold circuit and of the residue from the reverse-leach uranium circuit were taken on two occasions about one month apart, and on the first occasion a sample was taken of the residue from the low-grade, non-acid-leach gold circuit. The results can be summarized as follows.

(1) The high-grade samples showed definite adsorption at pH 11,3; at 0,03 per cent CN and pH 8,2; and at 0,01 per cent CN and pH 1,8. At pH 10,5 and 0,03 per cent CN and at pH 9,7 and 0,02 per cent CN, no adsorption was detectable. The minus 45 μm fraction of both these samples showed detectable adsorption when the total gold in the solution was low (0,2 g/t), but the first sample showed significantly greater adsorption than the second. This fraction of the sample gave no detectable adsorption when the gold concentration in solution was higher than 2 g/t.

(2) Under conditions at which the first high-grade sample gave significant adsorption, the low-grade residue sample gave no detectable adsorption.

(3) All the uranium residues showed significant adsorption. The amount of adsorption tended to decrease with increasing pH, but was still significant at pH 11,6 and 0,03 per cent CN, and tended to decrease with increasing gold concentration. Tests on the minus 45 μm fractions indicated that the first sample adsorbed more gold than the second, and that gold adsorption was not detectable above a gold concentration of 2,3 g/t in solution.

(4) On samples that had been dried and sized, adsorption was only detectable on the minus 45 μm fraction.

(5) In no case was gold adsorption detectable at a gold concentration in solution of higher than 2 g/t.

These results were considered in terms of a probable adsorption isotherm of the form: (gold on solid) $=K$ (gold in solution)$^{1/n}$, where K is a constant and n is probably greater than 1. The results suggested that, for a gold concentration in solution of 8 g/t, the adsorbed gold would be about 0,1 g/t at equilibrium in the presence of the usual amounts of cyanide and lime.

EXTENSION OF DETAILED TESTS TO OTHER CIRCUITS

Residues or thickener underflows from both high- and low-grade and from single-stream circuits from eight mines were tested by the techniques developed in the previous study, but, to improve the precision of the results, 6 to 12 identical determinations were made for each set of conditions. All samples were aged for 7 to 37 days before testing, with a mean period of nearly 17 days between the time that the sample was acquired and the time it was tested for each of the 35 tests performed. The results under conditions that definitely indicated adsorption are given in Table I. There was no detectable adsorption on either Vaal Reefs thickener underflow in the low-grade circuit or on the high- and low-grade residues from Blyvooruitzicht. Several tests on samples from Durban Deep, E.R.P.M., and Western Deep Levels indicated no

TABLE I

RESULTS OF DIRECT ADSORPTION TESTS THAT INDICATED SIGNIFICANT ADSORPTION ON ORE SAMPLES

Sample	Final solution conditions			(Au*) final/ (Au*) initial in solution
	CN %	pH	Au p.p.m.	
Vaal Reefs high-grade residue	0,03	11,5	0,5	0,993
Vaal Reefs high-grade thickener underflow	0,03	11,4	0,4	0,989
Vaal Reefs low-grade residue	0,03	10,5	0,5	0,979
Vaal Reefs low-grade residue	0,02	9,7	1,7	0,988
Vaal Reefs low-grade residue	0,02	9,8	2,2	0,980
Durban Deep residue	0,03	11,5	0,1	0,996
E.R.P.M. residue	0,03	12,1	0,2	0,991
E.R.P.M. thickener underflow	0,03	11,8	1,3	0,992
E.R.P.M. thickener underflow	0,03	12,2	1,8	0,990
Grootvlei residue	0,03	11,8	0,2	0,993
Grootvlei thickener underflow	0,03	11,5	0,1	0,991
Kinross thickener underflow	0,03	11,5	0,7	0,987
Kinross residue	0,03	12,2	0,7	0,991
Kinross residue	0,03	12,1	0,3	0,991
F.S. Geduld thickener underflow	0,03	11,5	0,6	0,992
F.S. Geduld residue	0,03	11,6	0,5	0,989
W. Deep Levels high-grade thickener underflow	0,03	11,3	0,7	0,993
W. Deep Levels high-grade thickener underflow	0,03	11,3	0,5	0,987
W. Deep Levels low-grade thickener underflow	0,03	11,8	0,8	0,989
Harmony uranium residue	0,00	3,8	1,2	0,913
Harmony uranium residue	0,00	5,5	1,2	0,973
Harmony uranium residue	0,02	10,2	1,2	0,981
Harmony uranium residue	0,03	11,6	1,2	0,988

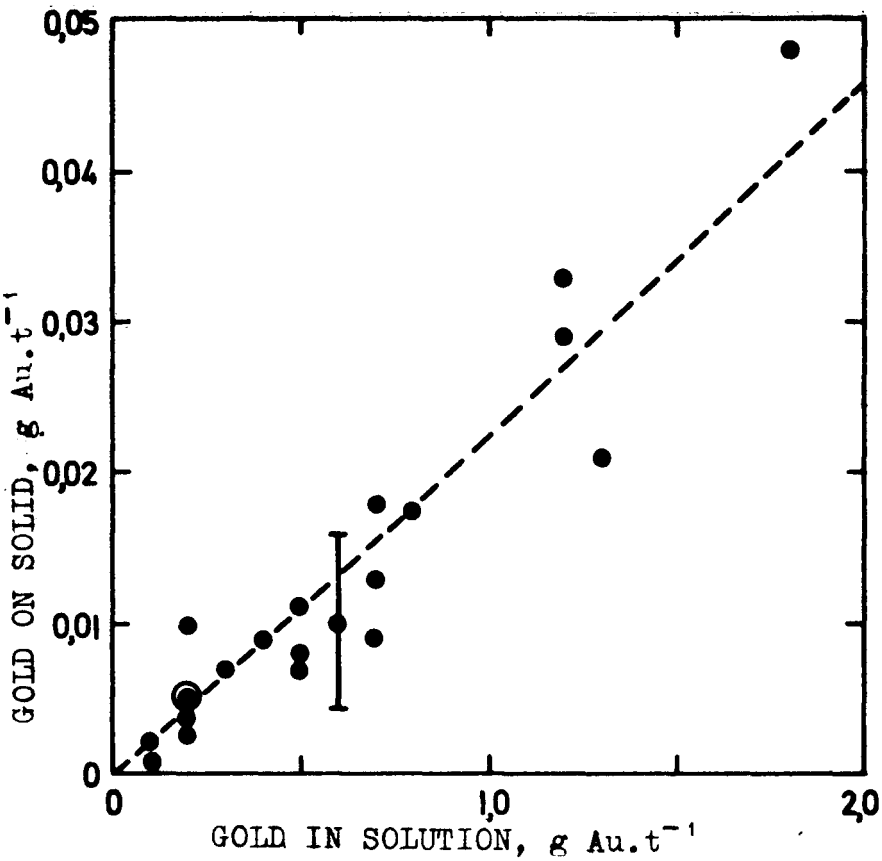

Fig. 3

significant adsorption under the solution conditions used in the tests —usually this was due to a gold concentration in the solution of higher than 2 g/t.

These results permitted the determination of the approximate nature of the adsorption isotherm. In Fig. 3, the gold adsorbed on the solid versus the gold in the solution is shown for all tests that gave positive results. Strictly speaking, this cannot be a valid picture, firstly because the points shown refer to various samples from a variety of sources, and secondly because the calculation of the gold on the solid involves a factor $(1-f)$ and, as $f \approx 1$, each point shown has associated with it a standard deviation of the same order of magnitude as the gold value on the solid. This is indicated on one of the points in Fig. 3 by a vertical bar. Nevertheless, it is apparent that there is a general tendency for the concentration of adsorbed gold to increase with increasing concentration in solution.

A qualitative picture could also be obtained of the effect of pH on adsorption. This is shown in Fig. 4, which indicates the tendency for adsorption to decrease as the pH is increased.

Consideration of the results leads to the conclusion that, for the typical ore, the loss of gold by adsorption is likely to be about 0,1 g/t for ores at equilibrium with a solution having a gold concentration of 8 g/t. An assessment of the experimental method and a statistical analysis of the results that the method yields shows that adsorption of this magnitude is very close to the limit of detection of the method. Accordingly, studies of a more sensitive but qualitative method were initiated.

THE RAPID CHROMATOGRAPHIC METHOD FOR THE IDENTIFICATION OF ADSORPTION CHARACTERISTICS OF ORES

The basis of the method is the formation of a thin layer of the material under test on a glass plate by careful spreading of a slurry*

*The slurry consists of the mineral to be tested, ground to minus 45 μm if necessary, slurried in a solution containing 0,05 per cent CaO and 0,035 per cent cyanide, the liquid-to-solid ratio being chosen to give an easily spread but moderately viscous paste.

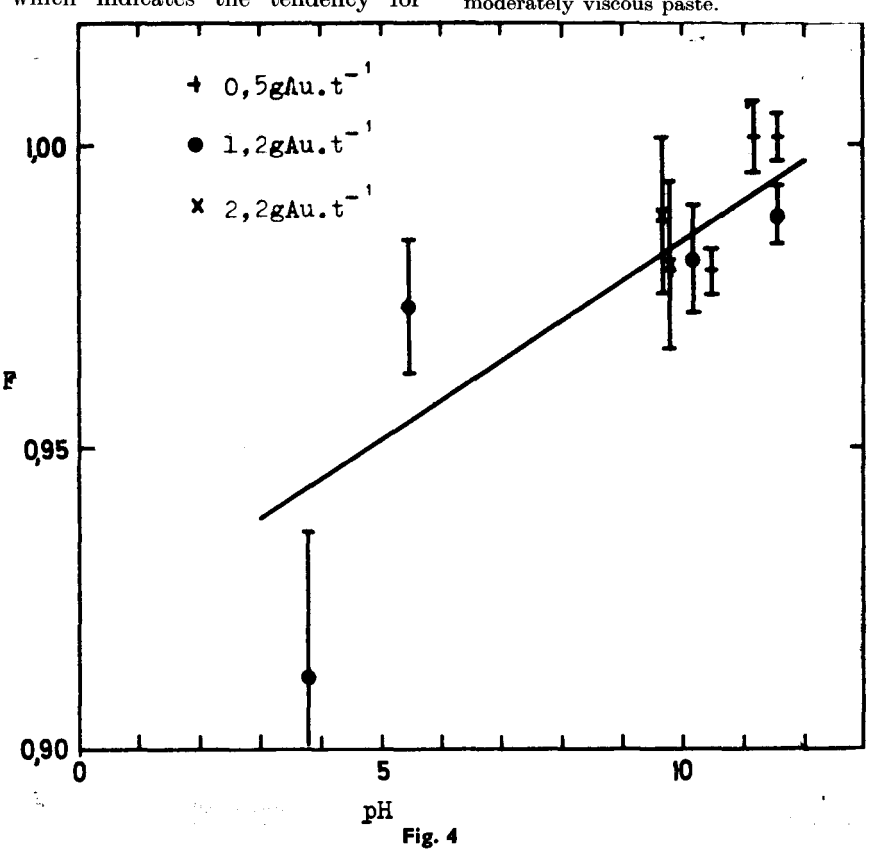

Fig. 4

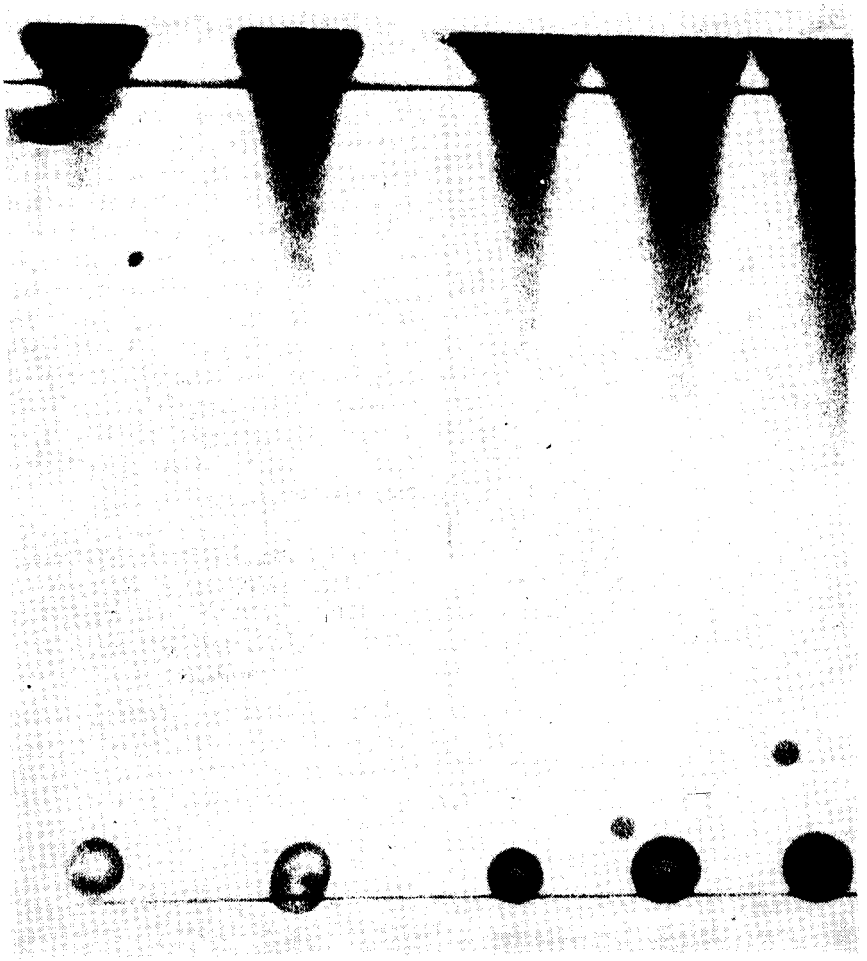

Plate I—Autoradiograph of gold on Kinross residue

and drying; the introduction of spots of radioactive gold solution (each of 1 to 10 μl) along a line 0,5 cm from the bottom edge of the plate; and the elution of the spot up the plate by immersion of the bottom edge in water, so permitting the solution to climb the plate by capillary action while the whole plate is kept in a water-saturated atmosphere to prevent evaporation. When the solution front reaches the top of the plate, the plate is taken out of the water-saturated atmosphere and dried in a current of hot air. The location of the radioactive gold is then determined autoradiographically.

This technique proved to be a sensitive method for demonstrating whether adsorption of gold occurred on the material forming the thin layer, and, qualitatively, the degree of adsorption. The autoradiographs given by this technique for Kinross residue, E.R.P.M. thickener underflow, and Blyvooruitzicht high-grade residue are shown in Plates I, II, and III. In Plate I, much of the original gold appears at the original spots, and the remainder is spread over the plate, with some concentration at the solvent front—a phenomenon referred to as "tailing". This indicates marked adsorption of the gold. In Plate II, there is slight evidence of the original spots and some tailing, which indicates little adsorption. In Plate III, some of the original spots have completely disappeared and there is no tailing, which indicates no adsorption.

There is a very close correspondence between the level of adsorption shown autoradiographically and that shown by the more direct method used in the earlier studies. This is indicated in Table II, in which a comparison is made between the results by the two methods.

The method was further tested on minerals that had been studied earlier. Plate IV is the autoradiograph of khaki shale—the marked tailing and definite original spots indicate very strong adsorption. In Plate V—the autoradiograph of Harmony pyrite—the "forward tailing" and very marked spots indicate very strong adsorption.

Table III gives a comparison between previous results by direct adsorption and the interpretation of the autoradiographs.

Because of the success and sensitivity of the thin-layer chromatographic technique, a preliminary investigation of the factors affecting desorption was undertaken. Plates VI, VII, and VIII show the effects of the following:

(1) The elution of Durban Deep pyrite at 20°C; The marked tailing and slight spots in Plate VI indicate strong adsorption;

(2) The elution of Durban Deep pyrite at 60°C; The moderate tailing and lack of spots in Plate VII indicate moderate adsorption; and

(3) The elution of Durban Deep pyrite three times at 60°C, the plate being dried in hot air

TABLE II

COMPARISON BETWEEN DIRECT ADSORPTION DETERMINATIONS AND THIN-LAYER CHROMATOGRAPHIC RESULTS

SAMPLE	Direct adsorption	Autoradiograph		
		Tailing	Original spots	Interpreted adsorption
Kinross residue	Definite	Marked	Marked	V. Strong
Kinross thickener underflow	Probable	Marked	Marked	V. Strong
E.R.P.M. thickener underflow	Occasional	Slight	Slight	Slight
W. Deep Levels low-grade residue	Occasional	Slight	Few	V. Slight
F.S. Geduld thickener underflow	Definite	Marked	Nil	Strong
Blyvoor high-grade residue	Nil	Nil	Few	Nil
Vaal Reefs low-grade residue	Nil	V. Slight	Nil	V. Slight
Vaal Reefs high-grade residue	Definite	Marked	Nil	Strong
Grootvlei residue	Definite	Marked	Nil	Strong

after each elution; The negligible tailing and lack of spots in Plate VIII indicate negligible adsorption.

These results may be considered in terms of the theory of thin-layer chromatography. In particular, it seems that tailing could imply a slow desorption process, and that the persistence of a spot at the origin probably implies a strong adsorption process.

TABLE III
COMPARISON OF THE ADSORPTION SHOWN BY VARIOUS MINERALS

SAMPLE	Direct adsorption	Autoradiograph		
		Tailing	Original spots	Adsorption
Quartz	V.V. slight, if any	Slight	Slight	Slight
Pyrophyllite	Strong	V. Marked	V. marked	V. strong
Khaki shale	Moderate	Marked	V. marked	V. strong
Chalcopyrite	Doubtful	No movement of spot		V.V. strong
Activated C	——	No movement of spot		V.V. strong
Harmony gravity concentrate	——	Forward	V. marked	V.V. strong
Merries gravity concentrate	Strong	Forward	Marked	V.V. strong
Harmony reef concentrate	Strong	Forward	Marked	V.V. strong
Durban Deep pyrite	——	Marked	Slight	Strong

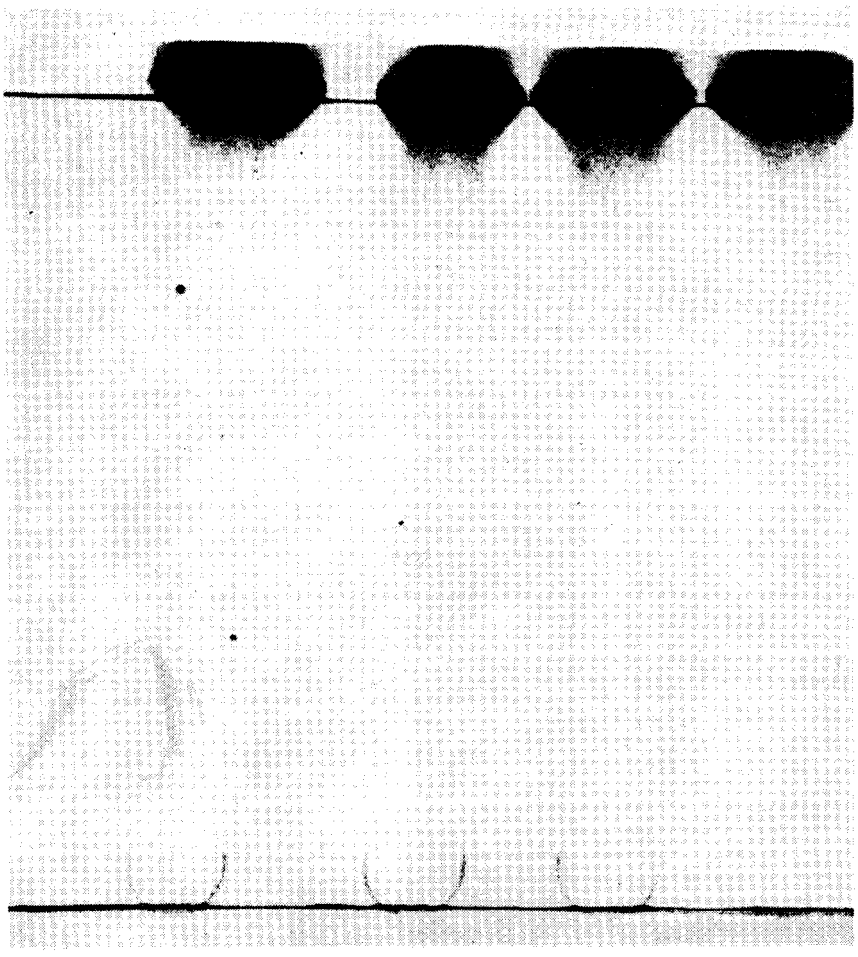

Plate II—Autoradiograph of gold on E.R.P.M. thickener underflow

DISCUSSION AND CONCLUSIONS

The results obtained in the study summarized above leave no doubt that adsorption of gold from solution onto constituents of the reef is a real phenomenon that gives rise to a gold loss from existing cyanide circuits of the order of 0,1 to 0,2 g/t at the concentrations of gold at present occurring in solution. Should richer ores become available (for example, by the wider application of selective mining methods), the concentration of gold adsorbed in the tailings may be expected to increase.

The present knowledge of the adsorption phenomenon can be summarized as follows.

(1) Adsorption is a slow, reversible process. To a first approximation, the kinetics of adsorption appear to obey a first-order rate law with a half-time of about 20 h.

(2) Adsorption is reduced and desorption assisted by an increase in the cyanide concentration in solution, but significant adsorption occurs at the cyanide concentrations common in plant solutions.

(3) Adsorption is increased by a decrease in alkalinity and pH. However, this may not prove a satisfactory means of controlling the loss by adsorption because increased lime concentrations in plant solutions may result in operational difficulties.

(4) Adsorption appears to be decreased by an increase in the temperature of the pulp. This may be either an equilibrium or a kinetic effect, but insufficient work has been done to indicate which is the primary effect.

(5) The heavy minerals in the reef show the strongest adsorption generally speaking, and clay minerals show a lesser degree of adsorption. For this reason, high-grade circuits, in which both heavy and clay minerals tend to be concentrated, show significantly greater loss of efficiency from adsorption than do low-grade circuits, other things being equal.

(6) There is an effect of aging after milling, whereby, the greater the time between milling and cyanidation, the less is the adsorption. This may be related to surface oxidation of the sulphide minerals in the heavy-mineral fraction. There are indications, however, that the adsorbing power of clay minerals increases with increasing time after milling.

(7) Some preliminary qualitative information indicates that the adsorption isotherm may be linear up to a gold concentration in solution of about 2 g/t. However, the failure to identify positively any adsorption onto reef samples when the gold concentration of the solution was higher than 2 g/t may indicate that the isotherm is in fact non-linear and that it levels off with 0,1 to 0,2 g of gold per tonne of solids once the gold concentration in solution is above 2 g/t.

(8) There is no indication that preliminary acid treatment of the ore, as in reverse leaching, reduces the potential for loss by adsorption. It seems more probable that the coating of gold during fine grinding is a better explanation for the results of the careful comparison between reverse-leach and conventional circuits described above, than is adsorption of gold.

ACKNOWLEDGEMENTS

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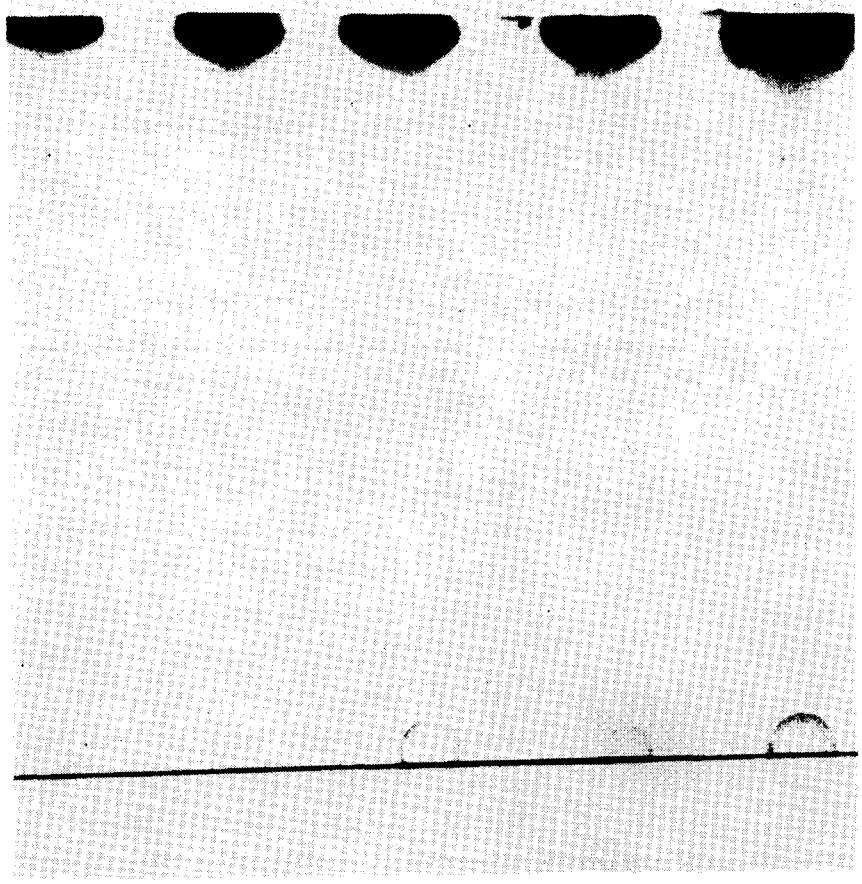

Plate III—Autoradiograph of gold on Blyvooruitzicht high-grade residue

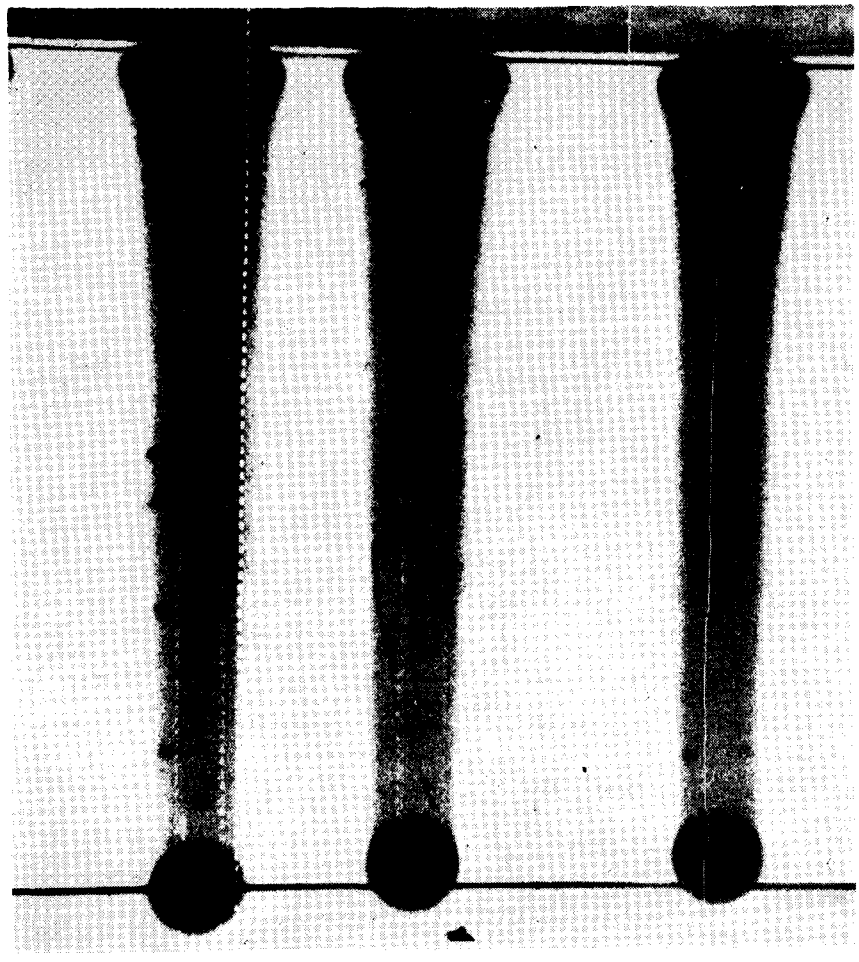

Plate IV—Autoradiograph of gold on Harmony khaki shale

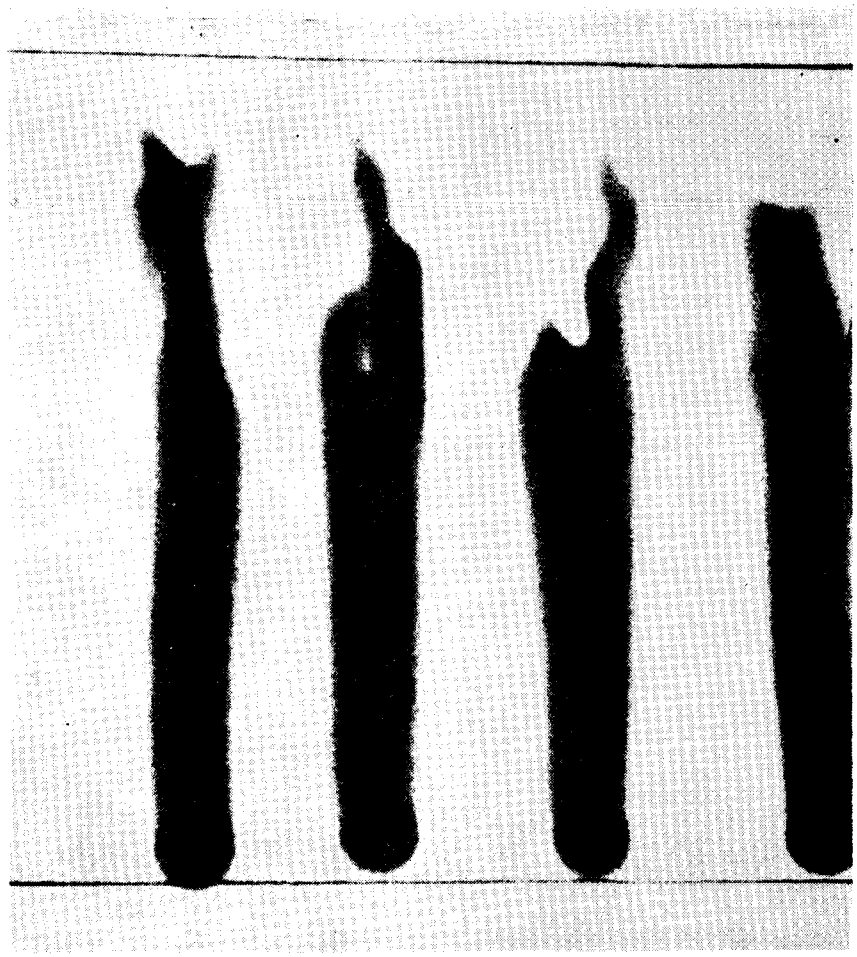

Plate V—Autoradiograph of gold on Harmony pyritic concentrate

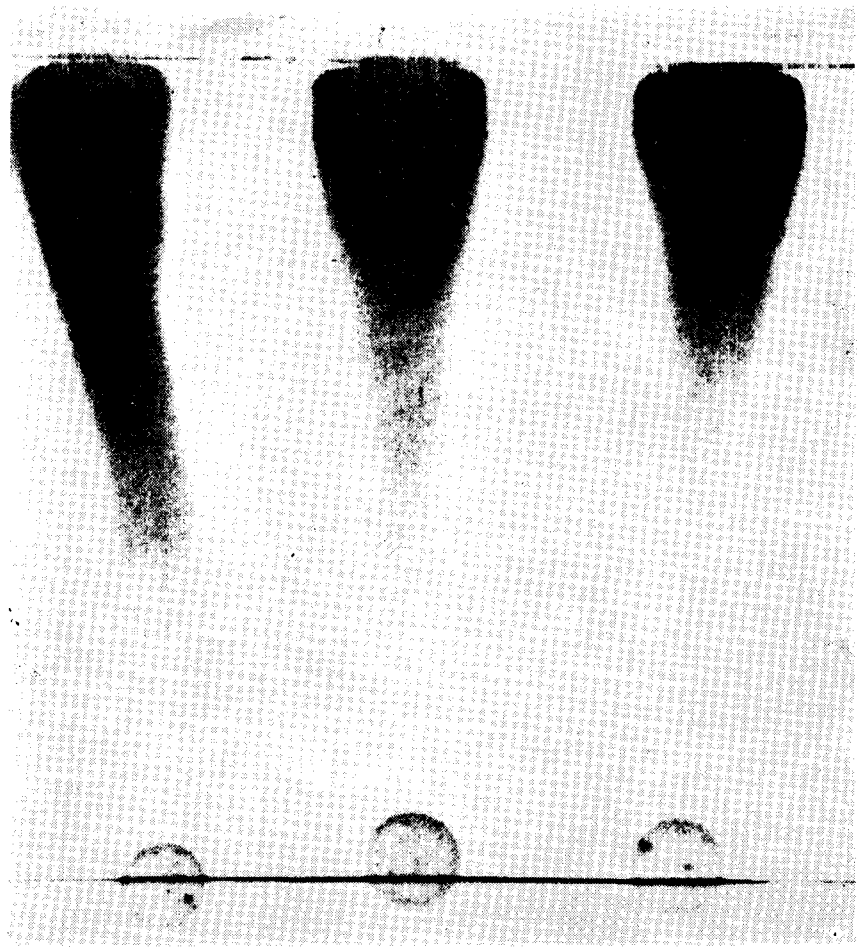

Plate VI—Autoradiograph of gold eluted once on Durban Roodepoort Deep pyrite at 20°C

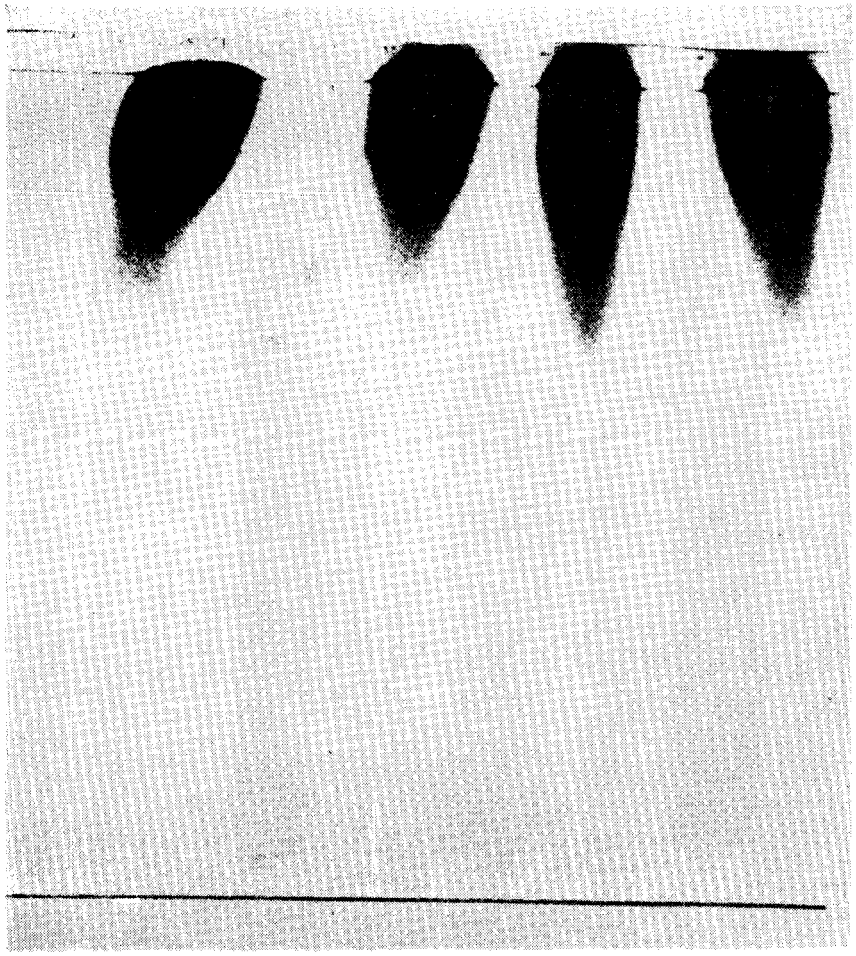

Plate VII—Autoradiograph of gold eluted once on Durban Roodepoort Deep pyrite at 60°C

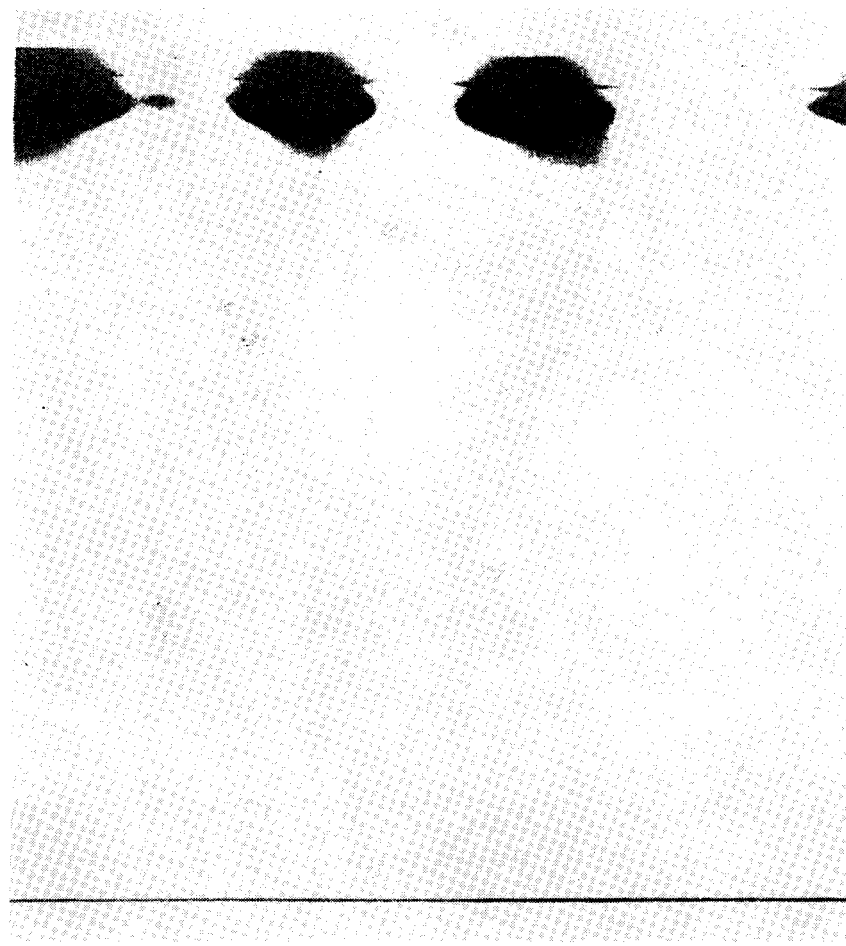

Plate VIII—Autoradiograph of gold eluted three times on Durban Roodepoort Deep pyrite at 60°C