

Author's Reply

Dr Hanekom

I would like to thank Dr Hanekom for a very valuable contribution; it summarizes careful statistical testwork which was an omission from the original paper. Minor manipulative details, the application of a finer measuring graticule and the reproducibility of the procedure are described and the author accepts with gratitude this ready-made answer to the first and second points of Dr Finkelstein's comments.

Mr Williamson

The author is indebted to Mr Williamson for historical background to early experiments with captive bubbles and it is conceded that the original paper described another avenue to an old flotation goal. The field of application is restricted and we would not work with all the material illustrated by Klassen and Mokrousov.¹ The particles in Figure 74(a) are far too large and irregular; material in Figures (b) through (d) could be employed for semi-quantitative work in spite of obvious disadvantages; Figure 74(f) represents ideal conditions. We have studied this mineral-collector association in the size range given and results were satisfactory. For larger pick-up values than that illustrated an induction period of more than 0.01 second was required (actually 90 seconds for a maximum bubble load at pH 7.2 with 25 g/t oleic acid!).

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1. KLASSEN, V. I. AND MOKROUSOV, V. A., 'An Introduction to the Theory of Flotation,' Butterworths, London, 128, Figure 74, (1963).

Mr Stander and Mr Kooij

Researchworkers in a practical mineral development laboratory may well ask what contribution yet another micro-technique can make to the problems of large scale ore flotation. The obvious answer is that there can be little or no direct translation of results obtained with a static system comprising air bubble and pure mineral concentrate to a dynamic multicomponent operation. However, for the rapid study of one mineral or variable some small scale apparatus must be employed.

In the Anglo American Research Laboratory, the described semi-quantitative pick-up technique has filled a niche and requirement. For ourselves, the system represents a definite advance over the contact angle approach in that samples of minerals conventionally prepared in laboratory or plant may be used, which is a desired step nearer flotation. We bracket this pick-up apparatus with the Hallimond tube^{1,2} and evidence is now to hand that pick-up curves may often be related to flotation recoveries obtained from this tube with pure mineral samples and from the Fuerstenau glass cell³ with the total ore at low pulp densities. We would not wish to push the comparison of pick-up results past this stage for there is much published development work relating the Hallimond and Fuerstenau equipment to flotation on a larger scale. At the Anglo American Research Laboratory for example, a test in a Fuerstenau cell is often the final integrated step in laboratory investigations into the TORCO process.

As these contributors rightly point out, pick-up tests can offer nothing towards the determination of optimum

reagent dosage for large scale flotation. This is the function of bench-type flotation cells with up to 2 kg batches of ore. At this level, collector performance and consumption and physical properties of the froth are more comparable with large scale operation. The pick-up cell, Hallimond tube and Fuerstenau cell are essentially equipment from which the effect of control parameters can be derived.

For the assessment of collector behaviour, the pick-up approach is rapid and economic and we offer here a pick-up contribution towards the flotation of Witwatersrand uraninite with anionic sulphonate collectors (Fig. 1). A large crystal of the local mineral was not available for contact angle measurements and owing to its low concentration in Witwatersrand gold-bearing reef, a small sample was laboriously obtained by tabling, superpanning and heavy medium separation. The pick-up values of a sized portion were determined by the described procedure in the presence of nine petroleum sulphonate collectors. Responses fell into two categories; "normal" curves (dotted lines) and a group of collectors which were very active at low concentration but showed depression of pick-up at the higher levels. The similarity in form of curves for collectors 1 and 3 was apparent and reagent 3 was found to be simply a diluent of 1. Otherwise, collector performance could not be related to either sulphonate content or molecular weight of the active constituent. However, reagent 2 gave the best performance in a bench flotation cell with regard to overall uranium distribution but, as predicted, reagent 1 yielded the best grades. Later pick-up tests with a similar class of collector have suggested that depression at high reagent concentrations may be due to "bubble armouring" whereby an hydrophilic air-liquid interface is produced which rejects mineral attachment.

Prolonged investigations with the same mineral sample have not been required except for the study of uraninite which lasted for more than a year. Variation in pick-up response could not be detected over this period during which the mineral was stored under distilled water. The only visible change was a small efflorescence of lead sulphate, readily removed and decanted off after stirring with a glass rod in the sample tube. In its main role as a "trouble-shooter", the pick-up method is applied to fresh mineral samples taken from a flotation plant and soon discarded or from a current run in the ore-dressing laboratory. After production of a concentrate, a solvent cycle, as described in the original paper, may be required to remove heavy organics or other contaminants as when a sample has been taken from circuits containing detergents, grease or return flotation solutions. This solvent cycle will not remove chemisorbed collectors and we prefer not to work with minerals from flotation tailings or with pick-up cell discards.

It has been thought preferable to answer the contributors' other apprehensions with regard to sample preparation, activators, depressants and the physical properties of reagents in another paper on offer to this Journal. It covers pick-up investigations relating to the flotation of nickeliferous pyrrhotite at two Anglo American Corporation Mines, which approach seemed the correct orientation for a reply to another contributor to this paper.

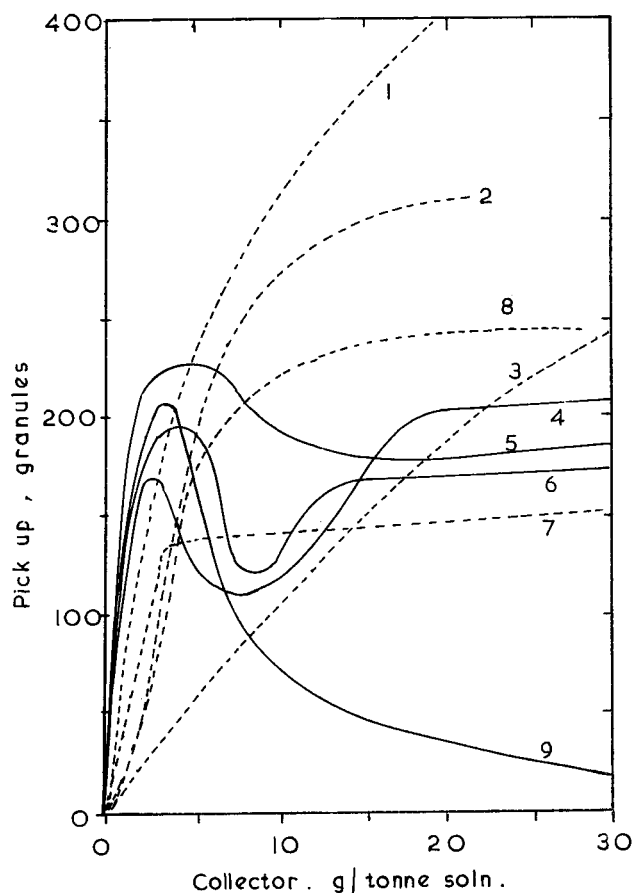


Fig. 1—Uraninite pick-up in the presence of a number of petroleum sulphonates.
 Minus 150 plus 200 mesh mineral. pH 4.5-5
 Curves 1-7 Acto sulphonates
 Curves 8-9 Aeropromoter 800 series

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Dr Finkelstein

An apology is due to Dr Finkelstein and his colleagues at the National Institute for Metallurgy. We approached him early in our search for microflotation apparatus and he advised us freely against the wide background of the Institute's studies. Later, when the pick-up technique was chosen and developed, we were unable to reciprocate because the first year's investigations concerned uraniumite and Company policy was against free dissemination of information. We are still not at liberty to discuss this very interesting development work. It is to Dr Finkelstein's credit therefore that with such meagre information at his disposal he was able to run parallel tests and be ready with his contribution upon presentation of our paper.

Dr Finkelstein has evidently examined this apparatus in the light of its possible application to fundamental flotation research and in this respect it is necessary to determine the reproducibility of the technique. Here, we must emphasize again that in spite of the environment in which it was developed, this pick-up technique has

fulfilled a "trouble-shooting" role only. During the pilot-plant flotation of uraniumite, problems were passed back to the laboratory which could not be solved in bench flotation cells, but pick-up tests were able to contribute materially by supplying pH ranges for collector attachment and estimates of collector efficiency. This approach has continued in other spheres and it cannot be denied that the sensitivity of the method has been good enough to yield unequivocal comparisons; for example the pick-up of pyrite in the presence of xanthate and dithiophosphate collectors or the effect of collector chain length on mineral attachment (original paper, Fig. 3 and 7). The values for experimental points given in all figures of the original paper were plotted as obtained and it was felt that if the scatter was no worse than that for Hallimond tube and Fuerstenau cell work currently published in international literature, the results would be acceptable.

Only qualitative observations can be made on the precision of the method which, it is admitted, must be determined for any application outside the above context. Reproducibility will vary with the mineral-collector system chosen; uraniumite and most anionic collector systems were found to be good subjects, the grain size and shape of the mineral being very regular and constant within the chosen size range; sulphide minerals and sulphhydryl collectors were well matched, likewise activated quartz and the amines by reason of strong bubble attachment and mineral regularity. These associations will yield the greatest precision but good reproducibility should not be expected from oleic acid systems or tests with organic depressants where physical changes in the reagent can result in irregular bubble loads; or with most collectors and gangue minerals, especially the micas, due to low hydrophilia and irregular shape of the particles.

We used a graticule ruled into squares with 0.5 mm sides and $\times 16$ optical magnification and normally combined these specifications with a minus 150 plus 200 mesh sample. Figure 2 of the original paper was drawn freely to scale, the bubble being therefore 2 mm diameter and the silhouettes were projected from an actual pick-up experiment. Some operators of the instrument prefer to measure the dark projected areas fractionally (for example, $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$ and so on); others favour a metric approach (0.2, 0.25, 0.4, 0.5, 0.75, 1.0). Our interpretation of the areas illustrated would be:

Collector concentration, lb/ton	Area		Particles
	Squares	mm ²	
Zero	—	—	2
1.01	0.82	0.20	46
0.03	2.58	0.64	155
0.05	3.50	0.87	204

We regret this estimation will not meet Dr Finkelstein's requirements. However, it is logical that greater precision should be obtained, at least at low bubble loads, by reducing the size of the grid used for area measurement concomitant with a similar reduction in grain size of the sample. For statistical work with a finer grid and mesh size, we refer to a detailed contribution from Dr. Hane-kom of the African Explosives and Chemical Industries Research Department. He found a coefficient of variation of 3.5 or less for a single test. As indicated in Dr Hane-kom's contribution there is a certain technique in the

operation of loading the bubble. For low bubble loadings, we merely dab the bubble into the mineral sample and wipe or roll the bubble over the mineral surface to achieve maximum loads when attachment is strong. We have found pressure to be a controlling factor only under conditions of "incipient attachment" and then the top of the bubble holder is gently tapped to dislodge mineral particles not firmly held at the interface.

As already explained, our choice of original material for publication was restricted and the disjointed residue could only be assembled in the chosen rather theoretical format. We are now able to offer in a separate paper, a pick-up study of nickeliferous pyrrhotite, which has practical implications but meanwhile within the abbreviated context of this reply a short pick-up investigation of a quite different nature is described.

We wished to study the application of a South African patent¹ to the flotation of hematite from a banded quartzite deposit in Swaziland. The patent claims, *inter alia*, the successful froth flotation of iron ores with alkyl sulphosuccinamates. The inventors admit that the collectors they proposed are surface active agents with high wetting powers ordinarily unsuitable for froth flotation. Further, the reagents exhibit the anomalous properties of being powerful collectors at extremely low concentrations while, at the same time and under other conditions, acting as dispersants for iron oxide slimes. "The reasons for this surprising and abnormal behaviour have not been determined, and it is not desired to limit the present invention by any theoretical explanation of the phenomenon", they state.

A minus 100 plus 150 mesh sample of iron-rich banded hematite quartzite gave the pH dependence curve shown in Figure 2 in the presence of 15 g/ton Aerosol 22. This activity in the acid range only was contrary to the claims of the patent but similar to the properties of a petroleum sulphonate collector. It was assumed that here Aerosol 22 was behaving as a normal anionic collector of this class. At pH 2.8, the effect of Aerosol 22 concentration on pick-up values for banded hematite quartzite was informative (Figure 3). With bubbles freshly extruded from the holder, pick-up increased with reagent concentration in the normal manner. However, when the bubble was held in the collector solution for two minutes after extrusion, but before mineral contact, marked depression of pick-up was noted at high collector concentrations and intermediate curves were obtained for lesser time intervals. The phenomenon fitted the theory of "bubble armoring" as proposed by Sutherland and Wark² and is related therefore to the wetting properties of the reagent.

This appears to be a definite advance in knowledge of the patent's application. Pick-up tests delineated quite clearly the separate collector and surfactant properties of the reagent. At low concentrations it is postulated, the sulphosuccinamate behaves as an ordinary anionic sulphonate collector; at higher concentrations the bubble interface can become wetted with time and the wetting properties of the reagent predominate by virtue of the large number of hydrophilic groups also present in the molecule. Further, the work is a rare illustration of Sutherland and Wark's proposal and of a type not available to them at the time of their publication.

This investigation is certainly incomplete but perhaps the pick-up instrument can be used by Dr Finkelstein in this way to delineate areas for further study in a flotation problem and as a preparative tool to obtain mineral samples in a known condition of collector activation for

study by more precise analytical disciplines such as infra red spectroscopy. This is one fork in the road along which we hope to travel.

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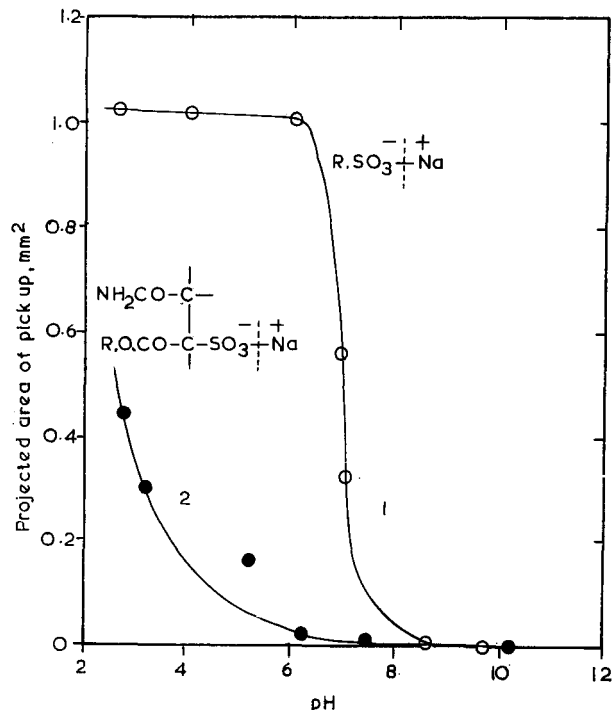


Fig. 2—Effect of pH on pick-up in the presence of a petroleum sulphonate and an alkyl sulphosuccinamate collector.

1. Plant-activated Witwatersrand quartz (minus 150 plus 200 mesh) and Acto 500 (10 g/t solution).
2. Iron-rich banded hematite (minus 100 plus 150 mesh) and Aerosol 22 (15 g/t solution).

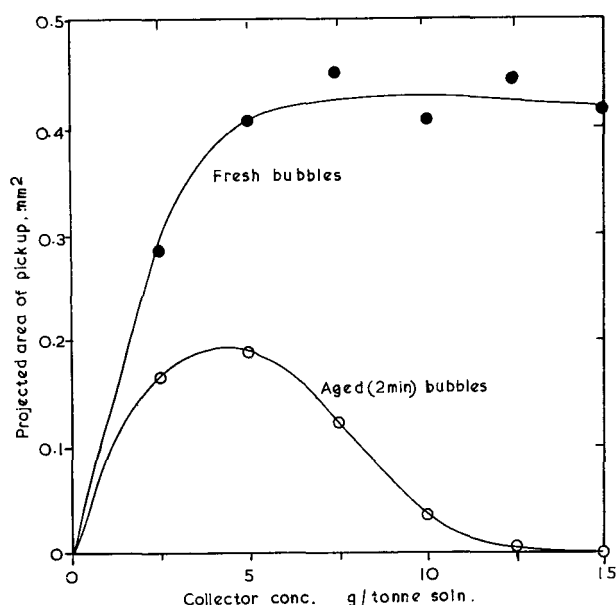


Fig. 3—Effect of bubble aging on the pick-up of banded hematite quartzite in the presence of Aerosol 22.

These contributors deserve thanks for their notes on the interpretation of results which are indeed relevant for, although the information in the paper was collated to demonstrate the scope of the pick-up technique, a certain validity was implied by the fact that most results could be made to fit the studies of other investigators.

With regard to the question of reproducibility, the quartz-laurylamine system (original paper, Figure 6) has been carefully re-examined and inflexions in certain pick-up curves again obtained (Figure 4). Whether these really exist depends upon the conviction of the investigator. P. L. de Bruyn¹ gives isotherms for the adsorption of dodecylammonium ion on quartz which can be similarly interpreted but he prefers smooth curves and firmly rejects the significance of the scatter of points at about pH 5-7, maintaining that absolute pH measurements around neutrality are not possible in unbuffered laurylamine solutions. Plateaux are to be seen also in some contact angle measurements made by R. W. Smith^{2,3} with dodecylammonium chloride and quartz at pH 5-8. This inconsistency in practical results is of no interest to ourselves but the opportunity has been taken to include in Figure 4 a pick-up curve for iron-rich banded quartzite from Swaziland. This curve follows closely that obtained by I. Iwasaki⁴ for Hallimond tube flotation of a similar mineral which, in turn, agrees with its electrophoretic response to pH. The low pick-up values for hematite should be noted when compared with the quartz samples. This comparison had a real and practical significance and in the laboratory this deposit has responded well to "reverse" amine flotation whereby quartz gangue is removed in the froth and a high grade hematite reports in the tail. However, as with most dynamic applications of pick-up tests, separation is not so clear-cut as defined in Figure 4 and caustic-starch is required as a depressant.

The pick-up curves for augite and calcium-activated quartz in the presence of oleic acid (original paper, Figure 5) were the result of two different investigations, but it was felt that their similarity merited some general explanation. Agreed, they do not follow the curve for copper-activated quartz given by Gaudin,⁵ who himself says that flotation of silicate minerals with soaps is related more to the activator than to the collector. He shows later that depression of flotation can occur as early as pH 7 if ferric iron is substituted for copper as activator.⁶ With regard to the reasons for depression, if chemisorbed oleate ions are bonded too strongly for replacement with hydroxyl ions, a compromise may be made and basic flotation compounds containing hydroxyl ions substituted, as proposed for example by M. C. Fuerstenau.^{7,8} It is quite acceptable that such depression could be enhanced by micelle formation but in the pick-up cell mineral aggregation follows this phenomenon whereby a mass of both hydrophilic and hydrophobic material adheres to the bubble and is recorded as false high pick-up values. This was not adequately explained in the original paper.

Pick-up curves with collector concentration as the variable often showed a common form indicating an early rapid rise in values to a subsequent plateau (for example, original paper Figures 3 and 4). A general theory was sought to explain this phenomenon and, in particular, the immediate attachment at very low collector concentrations. Plaksin's⁹ relatively modern work on variable coverage and coating densities came to mind and was more acceptable than the older theory of

complete mono- or multilayer collector attachment. The suggestion by Dr. Granville that pick-up curves fit Langmuir isotherms is quite acceptable to us, for there are at least two studies^{10,11} relating adsorption isotherms of this type to subsequent contact angle and flotation behaviour which is the kind of link we are seeking.

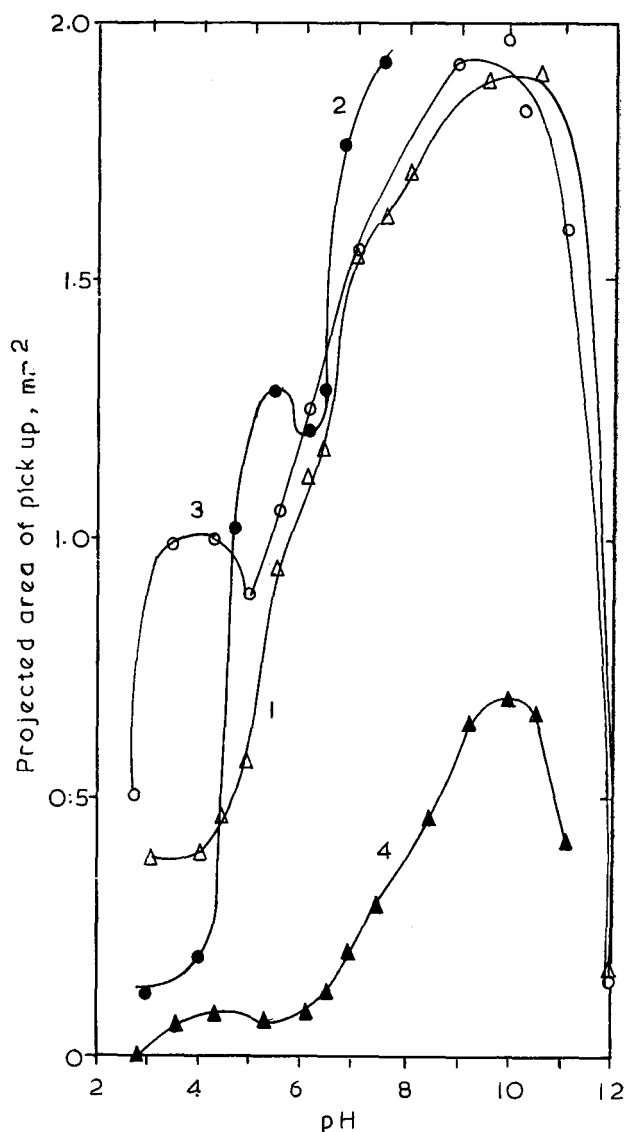


Fig. 4—Effect of pH on pick-up in the presence of laurylamine (2.5 g/t solution)

1. Quartz after leaching with hydrochloric acid.
2. Quartz activated with ferric iron.
3. Quartz activated in a Witwatersrand gold plant.
4. Iron-rich banded hematite.

Later pick-up work with TORCO copper has shown this substrate to be unique and highly amenable to xanthate flotation; the copper particles in the segregator discharge have an almost natural hydrophobic surface. We have found the TORCO copper-xanthate system to be more sensitive to pH adjustment in the pick-up cell than any other so far tested (original paper, Figure 5). Our obvious proposals to explain this sensitivity have been altogether too facile. We have found that when these active copper particles are placed in xanthate

collectors in the pick-up cell, colorations develop in the solution dependent upon xanthate concentration and pH value. Obviously this system requires much more study.

Ion exchange and mass action theories continue to be used to explain the structure of anionic collector coatings and hydroxyl depression at high pH values, particularly by some United States schools.^{12,13} Definitely, this is not the complete answer for cationic and fatty acid collector systems where physical adsorption seems related also to the surface and electrochemistry of the mineral.¹⁴

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