

A new bubble pick-up technique as a rapid flotation test method

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Discussion

Dr E. C. Hanekom (Visitor): Two years ago we used the bubble pick-up technique as developed at Anglo American Corporation for screening candidate flotation agents prepared in our laboratories. It was obviously necessary to know to what extent the technique gave reproducible results and a statistical evaluation of the test method was made using a mineral sample provided by Anglo American Corporation.

A bubble of 2.0 mm diameter was used and the measuring graticule was divided into squares (units) with sides of 5.0 mm at 25× magnification. The mineral granules had diameters from 53 to 74 μm. The bubble was loaded by depressing it against a layer of mineral grains to give an arbitrary but constant compression of 0.4-0.5 mm. It was rolled five times through 2 mm horizontal displacement. The bubble was then lifted, its load compacted by gently stirring and the projected area measured in squares (units) on the grid. Each substance was tested at 5 ppm concentration in distilled water at five points in the pH range 3-6.

With these standardized conditions of operation the reproducibility of the test was studied.

Four materials were tested and at each pH value the procedure of forming a bubble, picking up granules and counting the units was repeated ten times. From these results the standard deviation for a single count at any pH value was calculated for each material (Table 1).

TABLE 1

| Material | Mean | Standard deviation | Coefficient of variation (%) |
|----------|-------|--------------------|------------------------------|
| 1 | 21.92 | 0.72 | 3.28 |
| 2 | 22.01 | 0.76 | 3.45 |
| 3 | 21.03 | 0.62 | 2.95 |
| 4 | 23.89 | 0.76 | 3.18 |

The coefficient of variation of approximately 3 per cent was relatively low and it was decided that further refinements in the counting procedure would be of doubtful benefit with the present apparatus.

Similar experiments were carried out with 12 sample materials. In this case the bubble formation and pick-up were repeated four times at each pH value, the mean value was calculated for each set of four observations and final pick-up values for the materials were obtained by selecting the highest mean count. Each test was

completely repeated a number of times as indicated in Table 2 and the standard deviation calculated.

TABLE 2

| Material | Highest mean count (units) | Number of replications | Standard deviation (units) | Coefficient of variation (%) |
|----------|----------------------------|------------------------|----------------------------|------------------------------|
| 1 | 23.84 | 9 | 0.98 | 4.10 |
| 2 | 25.92 | 9 | 1.20 | 4.62 |
| 3 | 25.28 | 8 | 0.40 | 1.59 |
| 4 | 22.45 | 8 | 0.93 | 4.14 |
| 5 | 24.10 | 10 | 0.83 | 3.44 |
| 6 | 24.40 | 8 | 0.26 | 1.07 |
| 7 | 22.93 | 8 | 0.48 | 2.08 |
| 8 | 25.42 | 8 | 2.25 | 8.84 |
| 9 | 23.1 | 3 | 0.32 | 1.39 |
| 10 | 29.3 | 3 | 0.06 | 0.20 |
| 11 | 23.8 | 3 | 0.06 | 0.24 |
| 12 | 25.6 | 5 | 0.47 | 1.82 |

The results allowed the selection of the more promising materials and the rejection of poor performers at the 95 per cent confidence level. All tests were carried out by one operator. Some evidence was obtained that the method is sensitive to operator bias.

In conclusion it can be said that from all the results analyzed it would appear that once operation conditions are fixed (viz operator, pH control) the precision of the method is adequate.

The author wishes to thank Messrs African Explosives and Chemical Industries Limited for permission to publish these data.

G. S. Stander and **C. J. Kooij** (Visitors): We must congratulate Mr Lee for this most interesting and useful development of the pick-up experimental method. It certainly provides research workers with an instrument which makes flotation more of a science and less of an art. We visited Mr Lee at his laboratory where he gave us a demonstration of the bubble pick-up instrument and technique as developed and improved by him.

The most important application of this particular instrument in our opinion, will be in the field of evaluating different collectors for a given mineral under different conditions, as for instance, once a pure mineral sample has been obtained it would be relatively easy to determine the collecting properties of different collectors at different pH values.

As regards the determination of the optimum reagent dosage, the instrument will serve only to give an indication or trend as the volume of water is large compared with the volume of the mineral tested and it would, therefore, be impossible to determine the amount of reagent absorbed by the mineral.

When working with an ore containing various minerals it may be advisable to separate them and to determine the collecting properties of the particular collector on each of the minerals. From the information obtained it might be possible to determine the optimum conditions for the flotation of the minerals from the ore. This could be the case not only when separating the ore-minerals from the gangue, but also when separating different ore-minerals from one another. From experience it can be stated that it is usually better to float minerals separately rather than to have a bulk float and then to separate the minerals afterwards.

A definite advantage of the bubble pick-up instrument is that it can be applied to the study of the flotation of finely disseminated minerals when it is often impossible to collect a sufficient quantity of a particular ore-mineral for contact angle tests.

The main difficulties envisaged in the use of this technique are:

1. The isolation of the pure mineral concentrate, and the subsequent storage of the sample for prolonged periods which may cause contamination of the mineral particle surfaces by oxidation and other factors. Brief exposure of minerals to air in certain cases causes mineral particle surfaces to alter, and for this reason it is sometimes advantageous to add the reagents to the grinding mill. For instance, it is known from plant experience that the storage of ores containing pyrrhotite or chalcopyrite for relatively short periods of time may seriously affect the flotation characteristics of the minerals. Mineralogical observation has shown for example, that chalcopyrite from certain deposits may develop very noticeable tarnishing when exposed to the atmosphere for as little as a day or two.
2. In practice it is possible to get activation or depression of minerals by foreign ions; for example, quartz may be activated by grinding in an iron mill. These effects are ignored in the laboratory where glass apparatus and distilled water are used, and this is one of the reasons why laboratory results can sometimes not be duplicated in the plant.
3. When working with collectors like tall oils or amines which possess natural frothing properties it is possible that a collector may be selected which will cause frothing problems in practice. This problem can be serious when scaling up from bubble pick-up tests to the modified Hallimond tube experiments.

Dr N. P. Finkelstein (Fellow): Anyone who has had experience of the complexity of the flotation process,

of the multitude of variables involved and of the highly empirical way in which reagents are tested, processes developed, and plants controlled will appreciate the need for a rapid, reliable, and quantitative small scale test of the degree of floatability. At first sight it might appear to be a simple matter to devise a small scale laboratory test for floatability. And indeed over the last several decades many such tests have been proposed—techniques such as the Hallimond tube, the microflotation cell, the determination of contact angles, the phase inversion method, the bubble pick-up method. At the National Institute for Metallurgy we have tried most of these techniques with little success. We have not been able to find one which is reliable and quantitative, and one whose results are not critically dependent on the operator. We have been forced to discount the claims made for all of these techniques.

It is with a background of this experience, that I approach the work that Mr Lee has presented this evening. It is with this experience which makes me so confident that Mr Lee has made a very real advance in this field. He has shown that the quantity of particles picked up by a bubble and hence the degree of floatability, is directly proportional to the projected area which they occupy on the bubble surface; and, furthermore, that this area can be estimated using an eyepiece graticule. This, in my view, is the central point on this work. This is the piece of originality that makes the particle pick-up technique quantitative and convenient. This is the development for which Mr Lee must earn our unreserved congratulations.

The reason why I do not discount Mr Lee's method as I do the many other techniques that have been described, is that my colleagues and I have actually tested and applied his method. Despite the deep cloak of secrecy with which Mr Lee's work was surrounded, we were able to pick up a hint regarding the use of the eyepiece graticule for estimating particle pick-up, and immediately set out to test the idea on our own behalf. Using an apparatus very much like that described, we have carried out a programme of testwork, and as far as we can judge our experience confirms the claims made by Mr Lee. There are however, some points of detail where we differ, or where some amplification from Mr Lee would be helpful.

The first of these points concerns the grid against which areas were measured. Our apparatus employed a combination of magnification and graticule that gave us a grid 5 to 10 times finer than that shown in Fig. 2 of the paper. Could Mr Lee say if Fig. 2 is to scale? If so, would he perhaps say how he goes about making his estimates of areas using such a grid? The point is an important one. We would very much like to use a coarser grid, as estimating areas with fine grids is tedious and time consuming, but we do not see how such a grid can be used to obtain accurate estimates of a projected area.

The second point is the reproducibility of the technique. I find it surprising that the paper makes no reference to the reproducibility of the estimates which can be made using the method described. It is mentioned that the very tedious particle counting method was found to give a reproducibility of about 5 per cent. This is interesting, but nevertheless irrelevant. What really is required, is a measure of the reproducibility with which pick-up can be estimated by the use of the eye piece graticule. In our work at the National Institute for Metallurgy we have looked into this matter. We have made estimates of the amount of mineral picked up in

series of up to 100 tests using the seam stably conditioned mineral particles. We find the co-efficient of variation of an individual determination to be relatively high, about 25 per cent of the mean area. This means that 10 replicates will bring the coefficient of variation of the mean to 7 per cent which is a reasonable figure for most flotation work. Would Mr Lee please indicate whether he made a specific study of reproducibility, and how his results compare with ours?

My third comment concerns the technique used to bring bubble and particles into contact. We found that the quantity of pickup is to a large extent dependent on the pressure with which the bubble and particles are pressed together: in fact we believe the major source of irreproducibility in our measurements to be our inability to control this factor adequately. I should be grateful if Mr Lee would say whether he took any special precautions to regulate this variable and whether he too found it a sensitive variable.

Finally, I think it necessary to say that I am more than a little disappointed that Mr Lee has chosen to illustrate the application of his technique to problems of a fundamental nature. Quite frankly, the examples quoted do not in my opinion do justice to the potential of the technique. It is my belief that a technique of this nature cannot and should not be used as the sole basis for theorizing on the nature of the physicochemical processes taking place at the mineral water interface. The chemistry of flotation is too complex to yield to a single, very indirect technique. On the other hand, as I said in my introductory remarks, a convenient and reliable quantitative technique such as this would be of inestimable value for studies of more practical aspects of flotation such as the development of processes, the testing of reagents, or the control of operating plants. I believe that it was for such an application that the technique was developed in the Anglo American Research Laboratory, and that it is for such purposes that it is used in that laboratory. It would be of considerable value if Mr Lee or someone else from AARL could discuss the technique in the context of its application in practical studies, and if they were able to indicate in general terms the types of investigation in which they have found it to be useful, and what its limitations are. The question which is of great interest and which very likely their experience will allow them to answer is—how closely do the indications obtained by the technique agree with actual flotation results? How much reliance can be placed on the technique for the selection of reagents, and operating conditions? Have they in practical studies used it as a quantitative tool, or have they found it more useful as a 'go no-go' technique?

Mr President, let me sum up my remarks. The paper that Mr Lee has presented this evening is of the highest interest. There are points that I feel might be amplified. There are details of which I am a little critical. But these are indeed details. Regarding overall merit of the technique that has been developed, I have no reservations.

J. E. Williamson (Fellow): I should like to thank Mr Lee for giving us such an interesting description of a new bubble pick-up apparatus and for his discussion of its application in the examination of flotation fundamentals.

The captive bubble is an intriguing means of studying the surface tension and hence flotation effects at air-liquid-solid interfaces. Its use in a crude form, where the solid consisted of a polished face of a lump of mineral

certainly antedates 1930. In that year Prof A. F. Taggart¹ describes some experiments carried out with a captive bubble machine which permitted the observation of a somewhat enlarged image of the bubble on a ground glass screen. With this rather simple equipment he measured contact angles for galena using several collectors and frothers.

However, of even greater antiquity is a reference in the above paper to a demonstration of the application of the captive bubble to the picking up of small mineral particles. This latter demonstration was given in the course of the hearing of the case brought by Mineral Separation Limited against Miami Copper.

Since then these two techniques have developed from time to time as a scientific aid in the study of flotation phenomena.

The first technique referred to above depends on being able to prepare a large, smooth surface of the mineral under study. This in itself may present some major problems. In the first instance the surface must be perfectly flat and polished. This finish must, moreover, be obtained without the formation of any unwanted mono-molecular layer on the mineral. However, it does not take into account the fact that the mineral one wishes to study may not be available in large pure masses but only as fine grains. Nor does it take into account the effect of characteristic fragment or crystal shape. Neither does it allow for the effect of the specific gravity of the mineral.

The bubble pick-up would appear to overcome all of these shortcomings inherent in the captive bubble technique. It is, therefore, surprising that in over forty years so little had been done to develop equipment for applying this method.

Mr Lee's means of measuring the amount of pick-up in terms of projected area is interesting. This must expedite the task of carrying out determinations tremendously as compared to the tedious process of recovering and counting particles.

I would, however, like to ask Mr Lee whether he would feel safe in applying the projected area measurement to such a pick-up as one finds in Fig. 74 (a) and (b) of Klassen and Mokrousov². Here one sees particles of fluorite hanging from a bubble with their long axes normal to the bubble surface. Possibly some difficulty might also arise in the case of a micaceous mineral. Presumably a coefficient of weight or count to area would be desirable for each mineral tested. This is a minor point, of course, as most of the minerals tend to break into more or less equiaxed grains and can be expected to orient themselves in a common pattern on the bubble.

Mr Lee has illustrated the value of his technique as a means of evaluating the effect of reagent variables on the flotation properties of mineral grains. In this field it can well prove invaluable as a means of arriving at optimum conditions with a minimum expenditure of time and sample.

One can visualize other fields in which this technique will prove particularly useful. One of these is that in which one has only a small quantity of the mineral lost in a flotation tailing. Here one may laboriously recover a few grams of mineral by superpanning which, while too little for flotation in the conventional cell might be quite adequate for bubble pick-up studies.

This technique is a valuable new tool in solving flotation problems and used arm in arm with the laboratory flotation cell will expedite and simplify

flotation research and testing. However, it will never replace the flotation cell which provides means of studying the ore as it occurs with its complex relationships of sizes, minerals and mixed grains.

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Dr A. Granville (Member) and **Dr V. M. Lovell** (Visitor):
The problem of developing a rapid method for flotation testwork and one which is suitable for small amounts of mineral is one that is appreciated only by the worker in this particular field and the innovation introduced by the author of this paper deserves warm commendation. That the author has succeeded in making a worthwhile modification to a well-known technique is shown by the examples he has given. Although we appreciate that the information is intended merely to illustrate the application of the technique, we must query some of the interpretations offered.

The main difficulty is that we do not know how reproducible the results are. Therefore we cannot tell how significant are some of the experimental effects reported. For example, the suggestion is made that the pickup of quartz in the presence of laurylamine is due to the presence on the quartz of a film of iron oxide. However, this conclusion seems to be dependent on only one experimental point (Fig. 6, curve 1) and an error in pick-up of 20 per cent for this point would destroy the evidence for this conclusion.

If we regard the pickup curves as flotation recovery curves, the minima for oleic acid (Fig. 5 curves 2 and 3) are rather unusual and do not correspond to the information presented by Gaudin.¹ He reported that for quartz, activated with copper sulphate and floated by sodium oleate, the recovery stays high as the pH increases to 11, then drops sharply. The author of this paper attributes the high recovery at pH above 10 to micelle formation, but micelle formation is more likely to depress the flotation than to enhance it, since the formation of micelles prevents the collector from making the surface hydrophobic.² The cloudiness reported for the oleate systems at pH values above 10 is rather puzzling, because we found that 0.6 lb/ton sodium oleate solution is clear at these pH values. It only becomes cloudy when acid is added, or when a mineral is added which brings the pH below about 8. But it appears that the pH values quoted in this paper were measured after contact between the mineral and collector, and this would indeed be the logical way to do it.

The author explains the variation of pickup with concentration for pyrite in the presence of sec-butyl xanthate (Fig. 3, curve 1) by non-uniformity of adsorption. But this type of curve is a very common one for both physical and chemisorption even on homogenous surfaces. It is not even necessary that the adsorption potential decreases as the coverage increases. For

example, the simplest model which leads to this type of curve is the Langmuir theory, which depends on the assumption that the heat of adsorption remains constant.³

It is suggested that the decrease in pickup at low pH for the copper-coated Torco product in the presence of sec-butyl xanthate (Fig. 5, curve 1) is due to lack of the anion form of the collector. But this effect should not occur until the pH becomes much lower than 6. If we use the ionization constant of Hejl and Pechar⁴ of 5.3×10^{-4} for butyl xanthate (presumably the straight-chain isomer), then the dissociation equilibrium for the xanthic acid gives

$$\frac{(X^-)}{(HX)} = \frac{K_d}{(H^+)}$$

At pH 5 this ratio is 53, so there should still be fifty times as much xanthate anion as undissociated xanthic acid even at this pH.

In connection with the possible precipitation of copper xanthate at low pH values, we might just mention here that if the copper is present as cupric ions, then the cupric xanthate precipitated would decompose to cuprous xanthate and dixanthogen.⁵ So the dixanthogen may be responsible for at least part of the cloudiness observed. Nevertheless, the author's explanation of the decrease in pickup is possible unless the cuprous xanthate is adsorbed on the mineral. We would need to know the amount of xanthate precipitated in the liquid to decide whether this effect, together with the lack of dissociation of the collector, could explain the decrease in pickup below pH 6.

The author has invoked the ion-exchange theory to explain the decreased pickup by anionic collectors at high pH, but this theory has been hotly disputed for some time. It does not explain the fact that the same effect occurs with some cationic collectors, for example, chalcocite and sphalerite floated by isomyl amine, as described by Gaudin¹ or the pickup of pyrite in the presence of laurylamine as described by this author.

It has been held that oleate floats some minerals only if it is chemisorbed,⁶ and one would not expect strong chemisorption bonds to be affected by competition between hydroxyl and collector anions unless the mineral to hydroxyl bond were equally strong.

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