

A New Bubble Pick-up Technique as a Rapid Flotation Test Method

A. F. LEE*, B.Sc., (Member)

A pick-up apparatus capable of yielding quantitative results has been described. Studies of some collector-mineral systems have been presented to illustrate the versatility of the apparatus and prove the validity of results.

INTRODUCTION

The bubble pick-up approach to flotation is a small scale technique which appears to have been neglected by recent researchers. For the earliest pick-up experiments, very simple apparatus was employed which yielded only qualitative results^{1, 2}, and this lack of precision may have discouraged possible future investigators. The pick-up equipment presently to be described has been raised to the status of some contact angle apparatus which it approximates in precision under ideal conditions, in spite of the retained simplicity. As indicated by the results presented in this paper, the apparatus offers a new and promising avenue for the solution of flotation problems.

THE PICK-UP APPARATUS

The equipment consisted essentially of two groups of components mounted on an optical rail (Figs. 1, a, b, c.). The viewing and measuring arrangement was a binocular microscope [1] with the centre line of the optics in the horizontal plane. A pair of X2 objectives [2] and X8 eyepieces [3] were normally employed and a 0.5 mm × 0.5 mm graticule was inserted behind one eyepiece.

The sample [4] and flotation solution were contained in a rectangular spectrophotometer cell supported on a platform screwed to a vertically mounted mechanical microscope stage [5]. Vertical and horizontal cell adjustments could be made through screws [6].

An essential feature of the equipment was the bubble holder [7] which was a micrometer mercury electrode taken from a commercial polarograph³. It could be made to supply reproducible air-bubbles by half-emptying the reservoir and tapping the remaining mercury to the top of the tube. A test-bubble was readily produced by turning the micrometer head and was retained securely at the wide tip (5 mm diameter). The capillary bore (± 0.25 mm diameter) was not easily contaminated. The bubble holder was rigidly supported on its own mounting and stirrup [8].

An essential part of the apparatus was an accurate pH meter [9]. Stirring was provided through a conventional propeller shaft [10] and the cell was illuminated by a standard microscope lamp of variable intensity.

PROCEDURE

Estimation of the bubble load

During the early stages of the work, the loaded bubble was removed from the tip of the holder and the attached grains were counted under a microscope. This method followed somewhat that of Sun and Troxell^{4, 5} but avoided contamination of the bore of the bubble holder. The procedure was tedious but numerically low counts were reproducible to within 5 per cent.

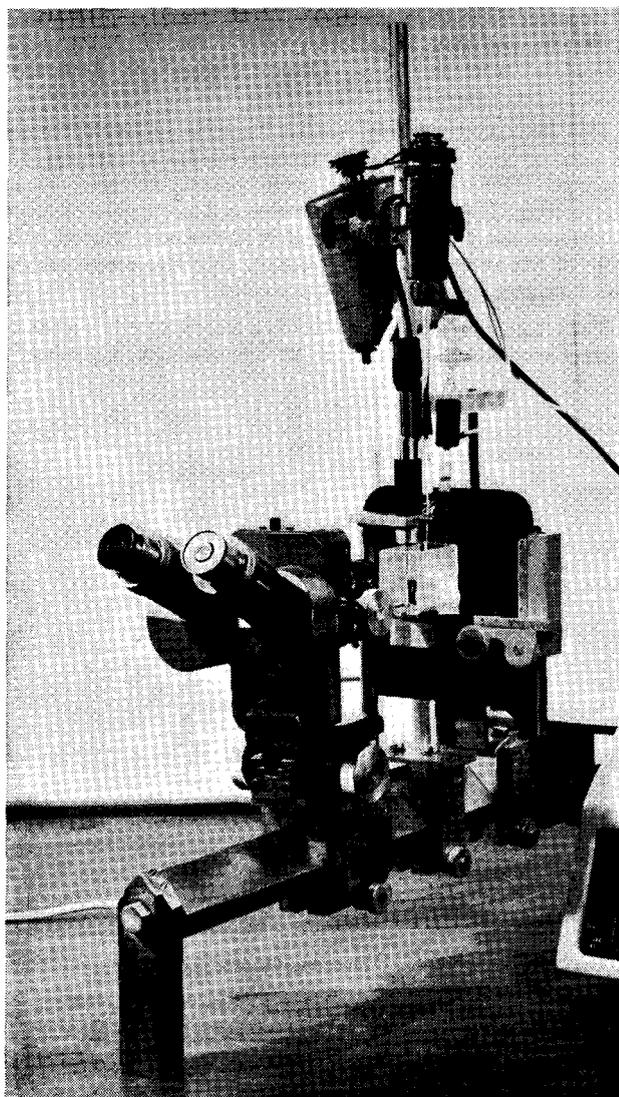


Fig. 1a—General view of the bubble pick-up apparatus

As the investigation progressed, it was noted that the mineral load invariably assumed a regular shape comprising a single layer of closely packed particles at the base of the bubble. An 0.5 mm × 0.5 mm graticule was inserted behind one eye-piece of the binocular microscope and at low intensities of illumination a silhouette of the bubble and its load could be obtained against the graticule as a background. The number of squares

*Anglo American Research Laboratory.

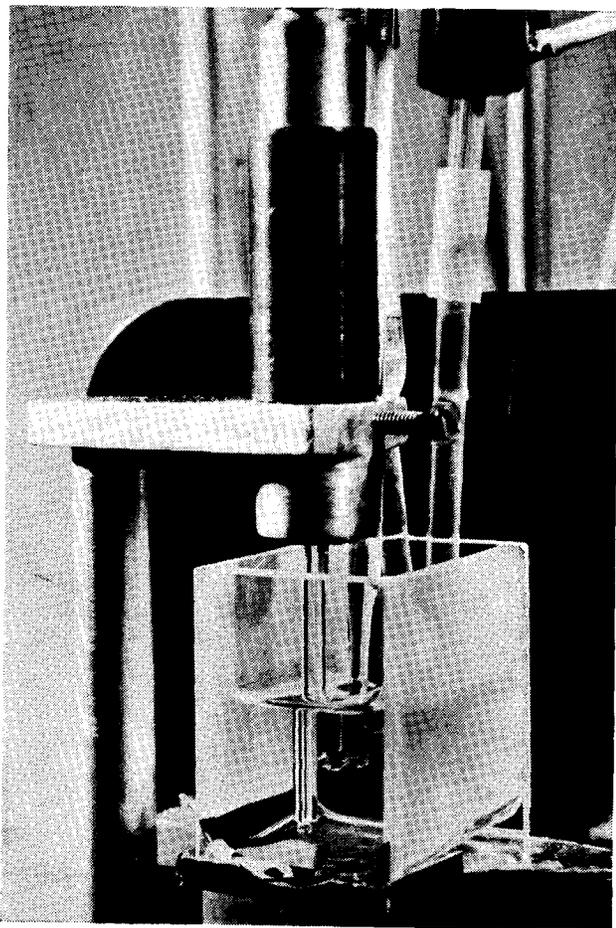


Fig. 1b—Close up view of the sample cell and bubble holder

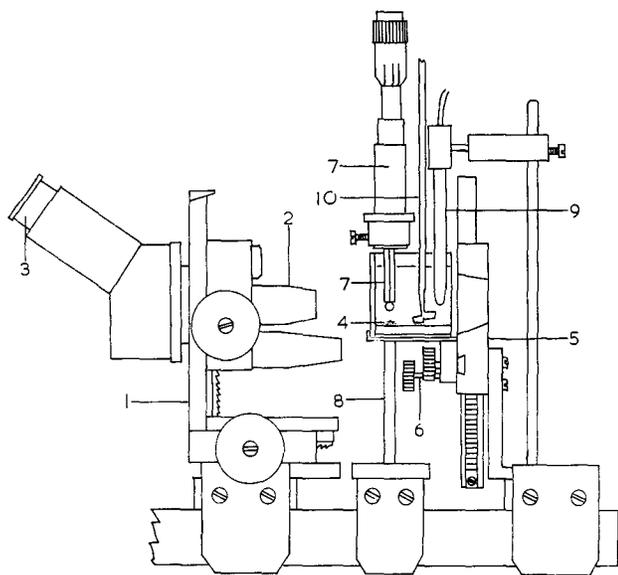


Fig. 1c—The bubble pick-up apparatus. General arrangement of equipment

covered by the load could be estimated, hence the cross-sectional area of the visible part of the pick-up surface could be derived. This value corresponded closely to the number of grains on the bubble determined by counting, and the use of closely sized samples permitted the construction of calibration lines. The method is illustrated in Fig. 2.

By strict control of such parameters as size of the air bubble and mineral particles, the determination of a pick-up index⁵ for each test was found to be unnecessary.

Sample preparation

Crushed mineral samples, normally screened to minus 150 plus 200 mesh Tyler, were dried and then soaked in benzene (twice) and acetone (once) to remove organic residues and flotation reagents. They were washed twice with ethanol (95 per cent), five times with distilled water and stored overnight under water before the first tests. Pyritic material was held under alcohol until ready for test.

In certain instances the samples were soaked for 24 hours in 10 per cent hydrochloric acid and rinsed thoroughly with distilled water. This treatment removed activating cations from the mineral lattice.

Test parameters

Two parameters were normally studied. The effect of collector concentration in solution was determined as follows: 20 ml distilled water were pipetted into the pick-up cell and about 0.01 g of sample transferred to form a small pile below the bubble holder. An air bubble (2.0 mm diameter) was extruded from the tip of the holder and the absence of any zero pick-up value was confirmed. An aliquot volume of collector stock solution (normally 0.2-0.4 ml increments of an 0.5 lb/ton solution) was added, and the mineral sample conditioned by stirring for five minutes. The bubble was pressed firmly against the mineral, held for 30 seconds and then withdrawn. The load on the bubble was determined, the bubble displaced and the sequence repeated after the addition of a further aliquot volume of collector solution.

The effect of the second important parameter—pH value of the surrounding solution—was determined subsequent to the addition of the required concentration of collector. Pick-up values were obtained following the described procedure after pH adjustments with 1.0 N sodium hydroxide or sulphuric acid solutions.

Special precautions

Before commencing a test the sample cell, bubble holder, stirrer and electrodes were cleaned by brief immersion in chromic acid solution, then thoroughly washed with distilled water. A symmetrical bubble which retained contact with the capillary of the holder usually indicated absence of contamination.

'Zero pick-up' in distilled water was essential, or a constant low pick-up with naturally floatable minerals.

New bubbles were formed after each contact with the mineral sample. Under certain conditions there appeared to be some concentration of reagent with time ('armouring') at the air-liquid interface.

THE EFFECT OF COLLECTOR CONCENTRATION

The results obtained for a selection of collector-mineral systems are given in Fig. 3. The form of the

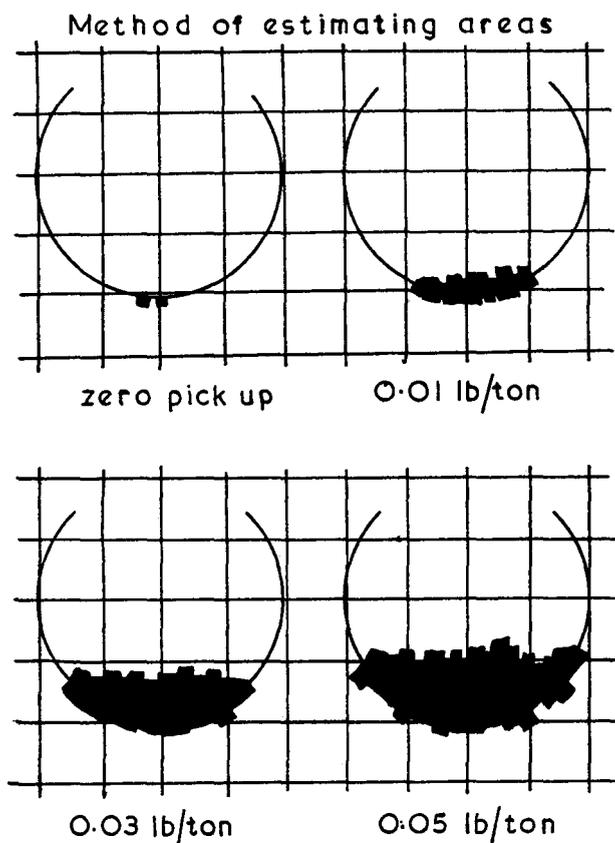
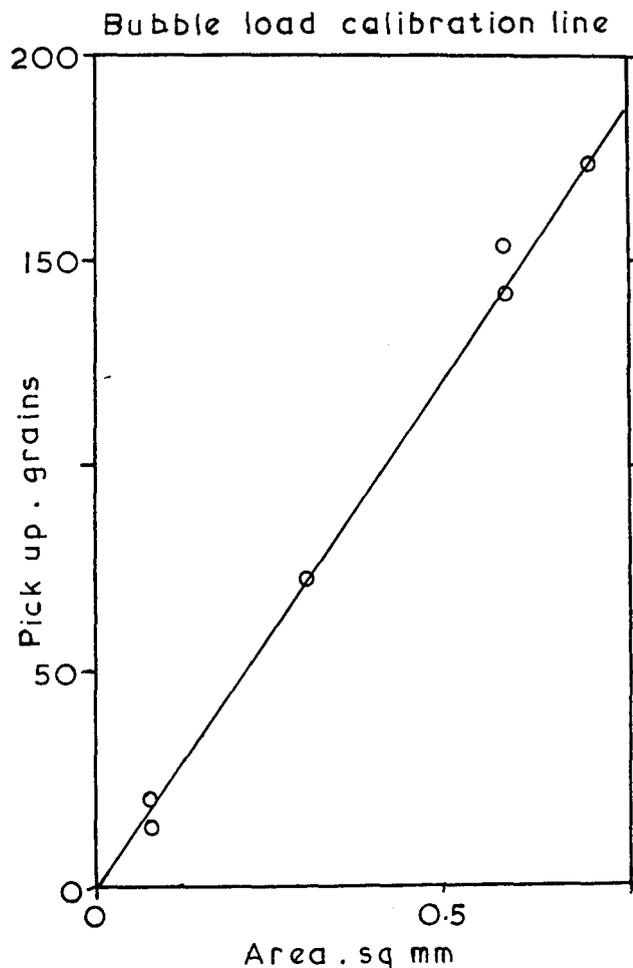


Fig. 2—Estimation of bubble loads for quantitative pick-up work



pyrite-xanthate curve (1) was typical and may be explained through modern knowledge of xanthate attachment to the heavy metal sulphides. Micro-autoradiography by I. N. Plaksin and co-workers⁶ has given visual evidence that the sorption of xanthate is not uniform. The coating is dense on some areas and on some mineral grains and spotty, or absent, on others. Presumably, those particles on which a sufficient layer density was first reached constituted the earliest bubble pick-up loads. Other particles became attached as the collector concentration was increased, and a rising pick-up curve resulted. Eventually, most grains attained a coating density sufficient for bubble attachment, and a plateau in the pick-up curve was usually obtained. Plaksin's later investigations have indicated that irregular chemisorption of collectors and cations might be the common condition. Indeed, most collector-mineral systems have yielded the typical concentration pick-up curve as for example, petroleum sulphonate and quartz activated by grinding in a steel mill (curve 4). Certain deviations from the final plateau condition may be due to physico-chemical reasons.

The two results for cresyl dithiophosphate (Fig. 3, curves 2, 3) corroborated the well-known practical application of this reagent to selective sulphide flotation. It was a good galena promoter, but pyrite attachment was poor in neutral to alkaline medium.

Cationic collectors

These reagents have been used for the flotation of both sulphide and non-sulphide minerals, and some investigations with laurylamine ($C_{12}H_{25}NH_2$) have been collated in Fig. 4. Activated quartz could be attached very successfully to an air bubble in the presence of this reagent, and the pick-up values were the highest obtained for any collector.

Depression of pick-up with increase in collector concentration was noted for pyrite and iron-activated quartz. A number of researchers have observed a similar flotation phenomenon with other collectors and have suggested theories to account for it. Sutherland and Wark⁷ have examined these proposals and have concluded that at the higher reagent concentrations, hydrophilic conditions pertain due to a collector species being doubly absorbed on the mineral surface or to an 'armoured' air bubble.

An important general deduction, arising from the investigations on the effect of collector concentration in solution, was that clean minerals were easily attached to an air bubble in the presence of very low reagent concentrations. Collector consumptions given on the usual pound per ton of ore basis are invaluable for material balances in the plant but the concentration of excess collector in solution appears to be a controlling

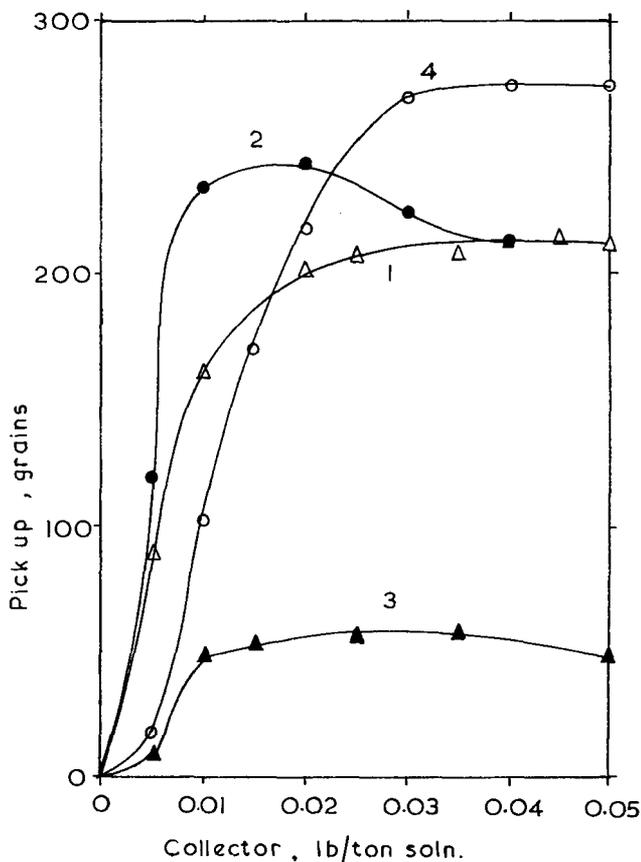


Fig. 3—Effect of collector concentration on some anionic collector-mineral systems. (1) Pyrite and sec-butyl xanthate at pH 6.5-7.5; (2) Galena and cresyl dithiophosphate (Aerofloat 25) at pH 6.5-7.0; (3) Pyrite and cresyl dithiophosphate at pH 6.5-7.5; (4) Plant activated quartz and petroleum sulphonate (Acto 500) at pH 4.5-5.0

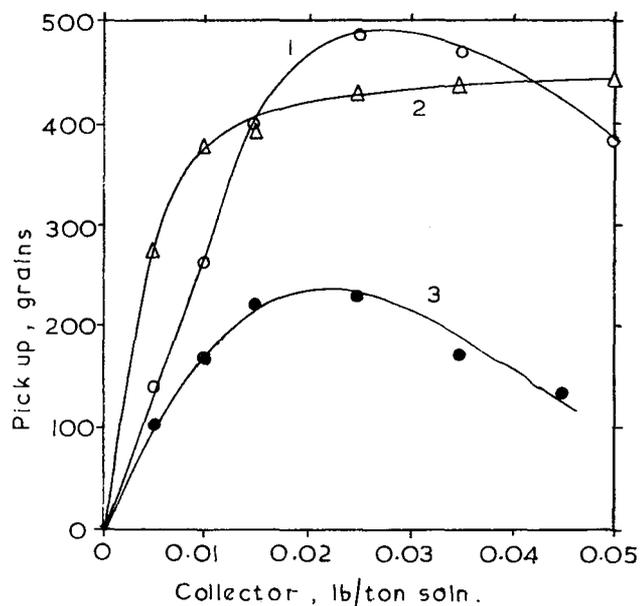


Fig. 4—Effect of laurylamine concentration on the pick-up of pyrite and activated quartz at pH 6.5-7.0. (1) Quartz activated with ferric iron; (2) Quartz activated with calcium; (3) Pyrite

factor, and the depressive effect of high concentrations has often been apparent in pick-up work. Russian awareness of this has been reported by I. N. Plaksin⁸ for a complex sulphide ore, while a very recent survey of xanthate residuals in solution in certain Australian plants has been given by Woodcock and Jones⁹.

THE EFFECT OF pH VALUE OF SOLUTION

Anionic collectors

The pH value of the environment can have a profound activating or depressing effect upon the action of ionizing collectors. Briefly, the concentration of active collector will depend upon the pH value of the solution, and the hydroxyl ion can displace most collector anions from mineral surfaces.

Pick-up tests offer a simple means for the determination of these effects as is well-shown in Fig. 5 (curve 1). The observed high pick-up values for the metallic copper present in this product at approximately pH 6 were expected, for it is known that alkyl xanthates are dissociated in weakly acidic or alkaline solutions. In this instance, depression of pick-up in alkaline medium due to collector displacement was accompanied by the appearance of a visible layer of cuprous hydroxide on the metallic particles. Conversely, in acid solution, collector inactivation was augmented by dissolution of copper from the metal surface followed by a reduction in xanthate ion concentration due to incipient precipitation of cuprous xanthate which clouded the pick-up solution.

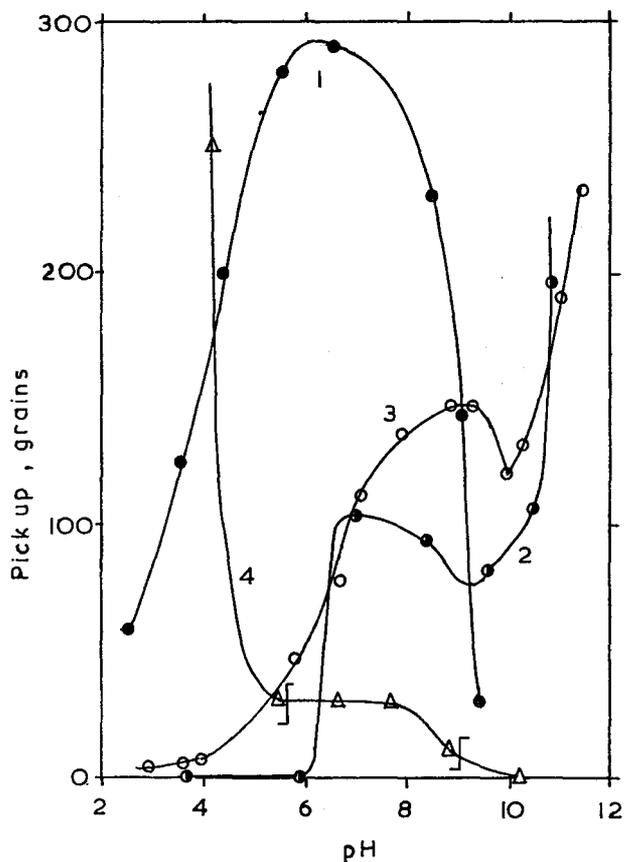


Fig. 5—Effect of pH on some anionic collector-mineral systems. (1) sec-Sodium butyl xanthate (0.06 lb/ton) and a copper coated Torco product; (2) Oleic acid mixture (FA-1, 0.6 lb/ton) and augite; (3) Oleic acid mixture (0.05 lb/ton) and activated quartz; (4) Monodioctyl acid pyrophosphate (0.02 lb/ton) and plant-activated quartz

The pick-up of augite and calcium-activated quartz in the presence of oleic acid (curves 2, 3) was somewhat complex but could be explained in terms of fatty acid chemistry. From visible indications, and the information of Fleming and Robinson¹⁰, lack of pick-up in acid medium was due to the presence of inactive oleic acid molecules. Strong pick-up at about neutrality resulted from chemisorption of the highly hydrophobic oleate ion and was followed by initial suppression through preferential hydroxyl absorption and oleate ion aggregation. This condition was rapidly reversed above pH 10, probably due to the formation of oleate ion micelles. In this region, the pick-up solution was cloudy and the mineral surface was coated with a visible layer of collector.

The alkyl phosphate collectors were found to be strongly active in acid medium (curve 4). In this instance, the pick-up response appeared to depend upon the behaviour of the collector alone. Increases in pick-up followed closely upon the release of an active anion, as indicated by equivalence points obtained by potentiometric titration of the collector. Theoretical considerations, and analytical data, suggested that the large increase in pick-up between pH 3 and 5 was due to the monoalkyl pyrophosphate in the mixture.

Cationic collectors

Controversy surrounds the attachment of amine collectors to mineral surfaces. Klassen and Mokrousov¹¹ have proposed adsorption of the collector cations in the electrical double layer surrounding the mineral, as suggested by their removal by one or more water washes. Taggart, Arbiter and co-workers^{12, 13} consider surface compounds to be formed between the free amine and the mineral in the case of sulphides and metals, and by an exchange chemical reaction with the collector anion in the case of quartz and other substrates.

In Fig. 6, consider quartz activated by grinding in the steel mills of a gold recovery plant (curve 1). The point of inflection of the curve corresponds with the zero point of charge of hematite (pH 7-8). At high pH values, the iron-activated mineral will be negatively charged and amine flotation is possible¹⁴. A similar curve for pyrite suggests that a surface film of iron oxide may be the active site for collector attachment. Severe depression at very high pH values might be expected as the concentration of active collector cation (RNH_3^+) is negligible above pH 11¹⁵, and the free amine does not appear to act as a collector even for pyrite. Klassen and Mokrousov¹⁶ note that in the flotation of quartz with laurylamine there is a definite optimum pH which does not coincide with maximum dissolution of the collector. The results reported here are also in agreement with their value of pH 10-11 given as the optimum for flotation of sulphides.

COLLECTOR STRUCTURE AND WATER REPELLENCY

Many collectors are heteropolar compounds and have clearly distinguished polar (solidophil) and non-polar (hydrocarbon) groups. The marked difference in structure and composition between the two parts permits separate examination of these properties in spite of the fact that they form a single ion. During the chemisorption of these reagents, the solidophil groups are attached to the mineral surface, and some properties of this bond have already been examined. The hydrocarbon groups are directed towards the aqueous phase and the mineral is rendered water-repellent by this collector orientation. The longer the hydrocarbon chain the greater are the dispersion forces set up between the groups, and the greater is the collector's water-repellent effect.

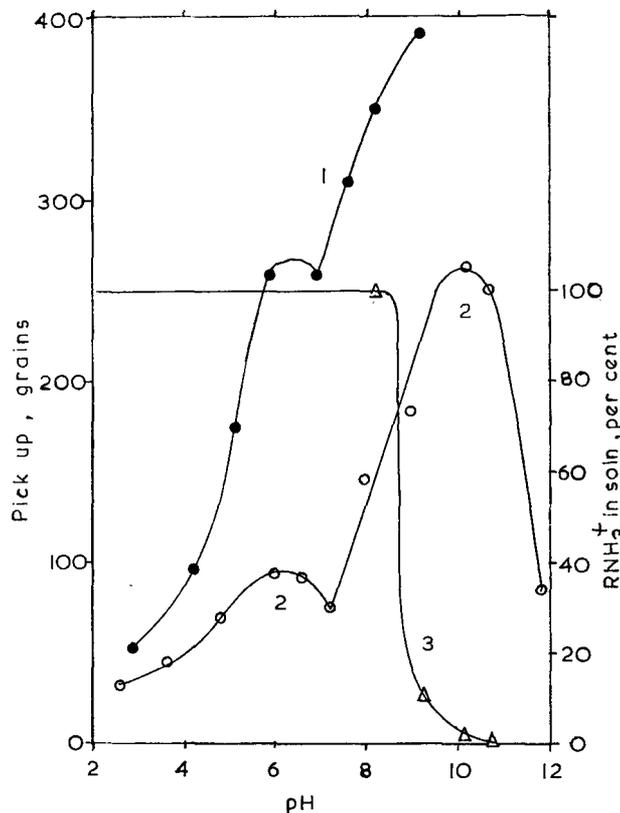


Fig. 6—Effect of pH on the pick-up of activated quartz and pyrite in the presence of laurylamine (0.01 lb/ton solution). (1) Plant activated quartz; (2) Pyrite; (3) Percentage amine ion in solution

Pick-up tests gave good indications of the relative water-repellencies of collector homologues (Fig. 7). Pick-up loads increased directly with the length of the xanthate hydrocarbon chain. This relationship has been plotted in a different manner in Fig. 8 and compared with information obtained from the xanthate-pyrite system. A curve for contact angles abstracted from A. F. Taggart's measurements¹⁷ for the same system has been added. Its conformation offered further proof of the validity of the pick-up work.

ACKNOWLEDGEMENT

Permission by the Consulting Metallurgist, Anglo American Corporation, to publish this paper is gratefully acknowledged; also the encouragement of the Directorate and senior staff of the Anglo American Research Laboratory.

REFERENCES

1. COOKE, S. R. B. and DIGRE, M. *Mining Engr.*, 1, 299 (1949).
2. COOKE, S. R. B., *ibid.*, 1, 306 (1949).
3. Mercury 'Kemula' Electrode, P 958 b, Radiometer, Copenhagen, Denmark.
4. SUN, S.-C. and TROXELL, R. C. *Trans. A.I.M.E.*, 196, 715 (1953).
5. *Idem.*, *Eng. and Mining Journal*, 158, 79 (July, 1957).
6. PLAKSIN, I. N. *et al.*, see Klassen, V. I. and Mokrousov, V. A., 'An Introduction to the theory of flotation,' Butterworths, London, 179-181 and 436-438 (1963).
7. SUTHERLAND, K. L. and WARK, I. W. 'Principles of flotation.' Australasian Institute of Mining and Met., Melbourne, 257 *et seq.* (1955).
8. PLAKSIN, I. N. and OKOLOVICH, A. N., *Flotatsii*, Akad. Nauk. S.S.S.R., Inst. Gorn. Dela., 26 (1965).

9. WOODCOCK, J. T. and JONES, M. H. 9th Commonwealth Mining and Metallurgical Congress, paper 4, Section 3, 1-30 (1969).
10. FLEMING, M. G., and ROBINSON, A. J. International Mineral Processing Congress, I.M.M., London, 960 (1960).
11. KLASSEN, V. I., and MOKROUSOV, V. A. 'An introduction to the theory of flotation.' Butterworths, London, 266 (1963).
12. TAGGART, A. and ARBITER, N. Min. Tech., 8, Tech. Publ. No. 1685 (May, 1944).
13. ARBITER, N., KELLOGG, H. H. and TAGGART, A. F. *Trans. Amer. Inst. Min. (Metall.) Engrs.*, 153, 517 (1943).
14. SCHONING, F. W. G. 'Iron ore flotation.' Joint Symposium on Chemical Engineering in Mineral Processing, University of the Witwatersrand, Johannesburg (April, 1969).
15. KLASSEN, V. I. and MOKROUSOV, V. A. 'An introduction to the theory of flotation.' Butterworths, London, Fig. 151, 265 (1963).
16. *Idem.*, *ibid.*, 267-8 (1963).
17. TAGGART, A. F., as reported in Glembotskii, V. A., Klassen, V. I., and Plaksin, I. N. 'Flotation.' Primary Sources, New York, 101, (1963).

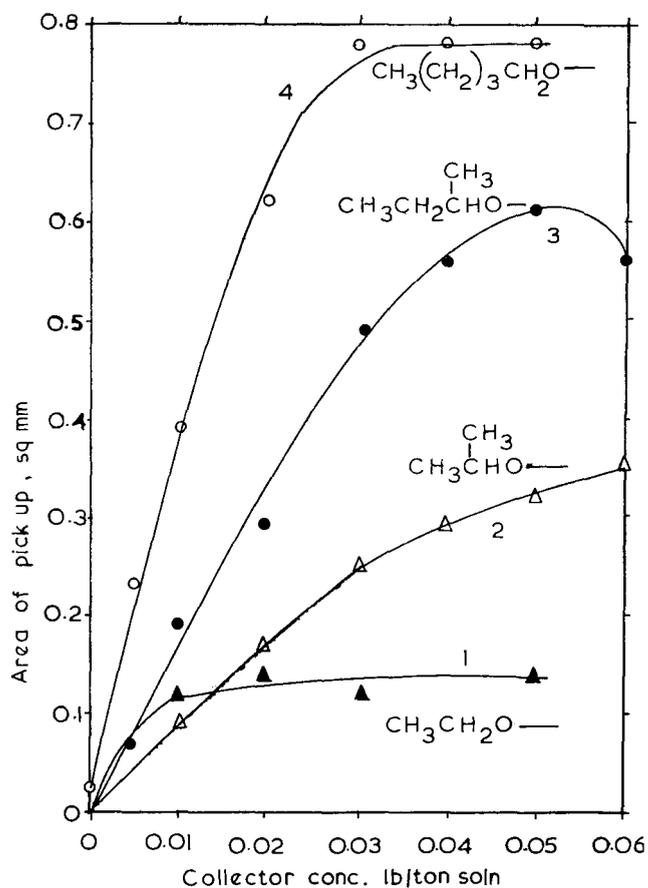


Fig. 7—Effect of chain length on xanthate pick-up of copper activated metallic particles at pH 6-7. (1) Potassium ethyl xanthate; (2) Sodium isopropyl xanthate; (3) Sodium sec-butyl xanthate; (4) Potassium amyl xanthate

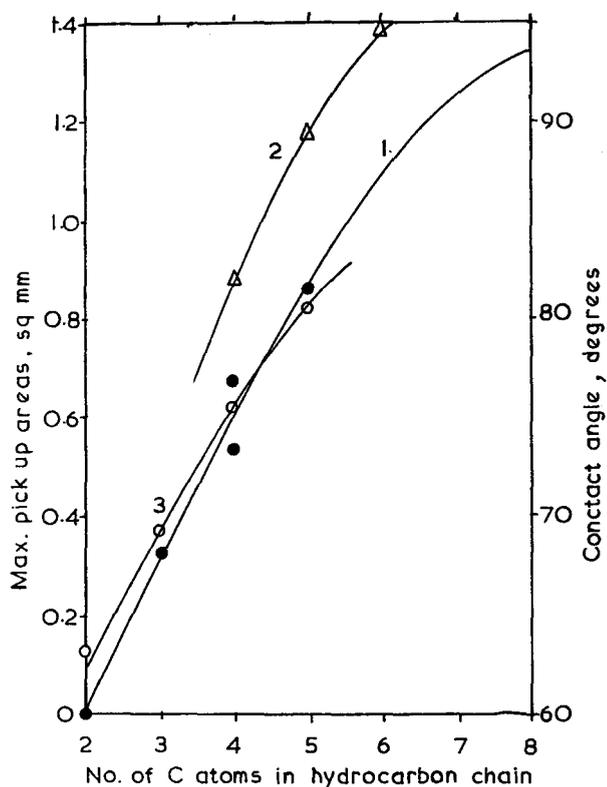


Fig. 8—General effect of xanthate chain length on pick-up. (1) Contact angles, A. F. Taggart; (2) Pyrite; (3) Copper-activated metallic particles