Role of Characterisation in Mineral Separation by Froth Flotation

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ABSTRACT

The paper emphasises the rationale behind characterisation in mineral separation by froth flotation. Inspite of the vital role of characterisation in mineral engineering, the entire global effort in this area is weak. Without adequate characterisation one can not understand the system under consideration and the reproducibility of the data collected in an incompletedly characterised system will be always questionable.

The importance of characterisation in the context of froth flotation has been discussed under six headings namely, solid phase, aqueous phase including solutes, gas or the second liquid phase, the three kinds of interface & interline, flow & force parameters and end products. Examples have been cited based on author's own work and also from literature.

Key words : Characterisation, Froth Flotation, Interfaces, Flow and Force parameters.

INTRODUCTION

The research activities in mineral engineering can be categorised under four headings: (a) characterisation (b) micro-process studies (c) macro-process modelling (d) feasibility studies and design. In India, considerable work has been going on in the third and fourth sectors and not so much on the second which includes molecular studies. The entire global effort on the first category is weak and unsatisfactory even though that constitutes the pivot on which other categories rest. The present author had quoted earlier[1] — "The basic dictum of scientific research is reproducibility or falsifiability, and how can a claim regarding experimental results on an incompletely characterised system be verified or refuted ... Yet in the area of processing of low grade ores, the standard of characterisation is indeed mediocre to put it mildly.

The above theme may be expanded in the context of froth flotation of minerals. The characterisation may be discussed at different levels :

1. Solid Phase
2. Aqueous Phase Including Solutes
3. Gas or the Second Liquid Phase
4. The Three Kinds of Interface and Interline
5. Flow and Force Parameters
6. End Products and Conclusion.

SOLID PHASE

The characterisation of the solid phase is most important because it is heterogenous and no two feed samples are indentical. The problem starts even at the geological macro-level. The same ore deposit varies in composition from point to point. To characterise an entire body is thus a gigantic task which are attempted by oversimplifying through the data of a representative sample whatever that means. It is like characterizing a nonspherical particle in terms of 'one' size!

The researchers are concerned with elemental as well as mineralogical composition, grain size distributions, locking-pair combinations etc. at the gross level of the ore - body as well as the comminuted product level. As the particle size comes down in the successive levels of comminution, complexity increases furthermore. A single particle is almost always heterogenous. Even if it were homogenous, the mind-boggling problem of 'size' and 'shape' are always there since it is rarely spherical.

The particulate system must be characterised not only in terms of gross chemical composition but also impurity content (ppm or even ppb level), phase composition (through diffraction studies-and all these informations are needed down the range of nano-meter size grains since we have entered the era of fine particle technology. One also needs information regarding valency states (of copper, iron etc.) functional groups, surface reactivity etc. So that these may correlate with the end results of froth flotation.

In fine particle technology, conventional microscopy and mineragraphy are hardly adequate. To characterise sub-micron particles and grains, often unliberated, one has to resort to electron microscopy which permits, in its latest stage of development, a unique combination of (a) phase characterisation through diffraction (b) micrographic and

(c) spectroscopic/chemical (EDAX/microprobe) facilities. The electron-microscopic, diffraction and spectroscopic techniques and their applications in mineralogy and mineral processing have been extensively review by Kumar and Ray[2]. Specifically they have described (i) bulk characterisation of minerals and their aggregates by TEM, SEM, EDAX and EELS (ii) spectometry for trace element analysis by SIMS and PIXE (iii) local structure determination by Mössbauer spectroscopy and XAS and lastly (iv) surface characterisation by AES, XPS, STM, LEED, IRS, LIMS etc.

The advent of recent semi-automatic equipment like QEMSEM had made it possible to provide quantitative measures of liberation in samples of different sizes, at different sections (such as roughing, scavenging, cleaning and regrinding) and for different components such as galena, sphalerite, pyrite[3]. Such studies characterise and explain the specific role of each unit operation.

Since Kai Siegbahn's pioneering work, photo-electro spectroscopy (PES) has been a very powerful tool in surface studies, contrasted with bulk or in-depth information. Because of the short escape depth of the excited electorns, information can be obtained from a quasi-surface layer of some 5-20 A° thickness containing impurity atoms. A general picture on molecular bonding, radicals, atoms and their valency states may be derived through the use of the family of the PES techniques such as ultra-violet PES or UPS, X-ray induced XPS, also called ESCA (electron spectron spectroscopy for chemical analysis, useful for surface analysis) X-ray fluorescence, Auger electron spectroscopy (in which outer electrons falling into vacancies emit secondary auger electrons) etc.

S. Chander and V.N. Sharma[4] showed, while investigating nickeliferous laterite from Orissa, the complementarity of the Mössbauer spectorscopy and ESCA techniques : While the former showed iron existing essentially as Fe^{3+} (in the bulk), the latter indicated a substantial amount of Fe^{2+} ions on the surface. Silver and copper atoms were detected on the tarnished ZnS surface only by Auger electron spectroscopy, and not by electron probe micro-analysis[5].

On electron micorscopic characterisation of Indian iron ores and deep sea manganese nodules extensive work has been done by Biswas et. al[6]. His last work was related to electron 'microscopic characterisation of synthesized wolframite minerals and their leach residues[7] '. Petruk

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and Sikka[8] performed a classic work on characterisation of Malanjkhand porphyry copper deposit in India. The detailed investigation relates to three ore types in the deposit : primary ore, moderately oxidized ore and intensely oxidized ore which have different mineralogical features and flotability properties and therefore demand different flowsheets for processing.

AQUEOUS PHASE INCLUDING SOLUTES

The collectors, frothers and additives used in the forth flotation system must be properly characterised. In the likely event that the xanthate used may be mixed and not pure, the relative proportions of the homologues-which have different collecting properties-should be ascertained. When soap is used as the collector, the corresponding mixed fatty acid needs to be characterised in terms of relative distributions in chain-length and unsaturation.

In one of the experimental investigations, Biswas et al[9] have characterised two commercial frothers : PPG3 and PPG 4 before use. The first was found to have two out of eight possible isomers of tripropylene glycol monomethyl ether: 99.7% isomer A and 0.2% B. The second frother sample used was tetrapropylene glycol monomethyl ether which contained 96.7% isomer X, 1.9% Y and 1.2%. Z from 16 possible isomers as envisaged from the point of view of stereo-chemistry. Does one have any logical basis to assume that different proportions of isomers in the frother samples (or homologues in collector samples) might not give different results? In the absence of such characterisation data what would be the utility of the experimental reports, their reproducibility in another laboratory and their scaling up in a process industry? Yet such reports abound in the literature!

Even the additives need to be carefully characterised. Khosla and Biswas[10] determined the molecular weight distribution of the tannin materials by gel permeation chromatography before these were used in calcite-fluorite separation by froth flotation. Archibald's ultracentrifugal analysis method was employed to determine the molecular weights of starch, amylose and amylopectin which were subsequently used in froth flotation and selective flocculation experiments[11].

One should know the quantities of each additive solute not only at the point of entry but also during the flow and after the experiment. Sensor technology is being developed to monitor residual concentration of reagents by spectroscopic, potentiometric (specific ion electrodes) and

voltametric detectors[12]. Advantages should be taken of these developments in the design of a feedback reagent control system. These would also help in quantifying the adsorption characteristics of the solutes which collectively determine the relative flotabilities of minerals.

GAS /SECOND LIQUID PHASE

Characterisation of the gaseous phase in froth flotation systems has been a relatively neglected field. Professor A.M. Gaudin of M.I.T. used to tell the present author that oily dirt in the atmosphere (such as near the confectionaries or petroleum industry) may reduce the selectivity in the flotation system through indiscriminate adsorption of oil on the solid surfaces. It was at the suggestion of Prof. Gaudin the present author established the positive effect of CO_2 in the atmosphere affecting flotability of calcite. Fundamental studies on the role of CO_2 (essentially surface-chemical reaction) in a calcite flotation system were conducted at IIT Kanpur[13,14].

In a calcite flotation system Tiwari and Biswas[15] established that the size distribution of gas bubbles is as important as the particle size distribution. High-speed photography was employed as a tool. For our specific collector-frother system, as the flow rate of air from 0.0482 to 2.41 l/min. was increased the bubble size distribution was changed from 0.6 - 2.5 mm. to 1.0-4.9 mm, the uniformity factor dropped from 6.75 to 2.28 and bubble surface area increased form 0.17 to 5.50 m^2/ min. The kinetcs of froth flotation was affected and could be attributed to the aforementioned variation of the parameters. Thus the importance of quantitative characterisation of the gas-phase was established which is often overlooked by the research workers. The role of micro-bubles is very significant in the context of beneficiation of fine particles.

In one of the studies Biswas et. al[16] replaced gas bubbles by droplets of a second liquid namely kerosene, and measured the droplet size as well as the collector concentration (sodium myristate) in the kerosene phase. For volatile collectors, their gas phase concentration should be measured in connection with the air flotation experiments.

THE THREE KINDS OF INTERFACES AND INTERLINE

Froth flotation depends upon : preferential adsorption of surface-active agents on specific minerals, lowering of surface free energy of the latter, attachment of air bubbles and levitation of the particle-bubble

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complex. Therefore, it is quite obvious that the interfacial properties, which are related to the bulk properties, directly influence selective flotation. Yet, the researchers who report flotation data, often neglect to concurrently measure and report these interfacial properties such as adsorption magnitudes!

The surface properties of particles are often so different from their bulk properties. Since trace quantities of Cu on sphalerite surface and of Zn on copper mineral surface interchange their flotation behaviour, there is a need to measure them. The present author has rarely come across instances of this aforementioned factor being incorporated in a statistical modelling exercise.

Adsorption of collector on the solid mineral surface is of crucial importance. Adsorption magnitudes in the three interfaces determine the respective tensions which are interrelated through contact angle. For solid (S) - water (W) - oil (O) system where oil droplet replaces air or gas (G), Smolders derived the relationship :

$$\frac{d(\gamma_{wo}\,Cos\theta)}{d\gamma_{wo}} = \frac{\Gamma_{so} - \Gamma_{sw}}{\Gamma_{wo}}$$

The author verified the premise in the equation that Γ_{so} should be greater than Γ_{sw} when $\gamma_{wo}\,Cos\theta$ versus γ_{wo} plot has a positive slope. Work on corundum and rutile as solids, n-dodecane and kerosene as oil, and C^{14} - tagged sodium myristate as surface-active agent[17] was demonstrated that adsorption at the interline $\Gamma_i > \Gamma_{so} > \Gamma_{sw}$ and Γ_i is of the order of monolayer coverage 6.6×10^{-10} mole/cm².

The old contention that adsorption at the *interline*, not accounted in the thermodynamic equations of Young, Gibbs and Smolders, is of supreme importance and necessitate the emergence of another genius like Gibbs working on interline thermodynamics still remain in 1998 as uncontested and unanswered.

The point that the author wanted to stress here is that the phenomenon of froth flotation cannot be rationally understood without characterising the adsorption behaviour of different solutes in the three kinds of interfaces and singular interline. Adsorption of frother is crucially important not only in the water-air interface but also on the two solid interfaces. The adsorption of the frother molecules on the solid surface, and their interaction with the collector molecules - both in the bulk as well as in the state of adsorption on the solid in the flotation system was measured[18,19]. Subsequently, Fuerstenau and Pradip[20] measured adsorption of frothers at coal/water interfaces[18].

The interfaces in the flotation system need to be characterised not only in terms of energetics (tension) as affected by adsorption but also of their electrical double layer properties. Solid surface potentials and bubble potentials must be accurately determined.

FLOW AND FORCE PARAMETERS

The factors so far discussed (already a large number!) pertain to the thermodynamic probability whether a specific particle may float in a well-characterised system. Some additional kinetic factors are relevant to determine whether the particle would actually float. The recently innovated column flotation may be viewed as a co-current liquid-liquid extractor for which equilibrium information and the knowledge of flow properties should suffice to determine the theoretical number of plates, and this has to be multiplied by the factor of plate efficiency.

The utilites of various dimensionless numbers such as 'Power', 'Flow', 'Froude', 'Reynolds' etc. in a typical flotation cell are sacrosanct, but unfortunately these parameters are rarely measured and reported by researcheres. Optimal flotation rate depends upon high degree of agitation around the shrouded impeller and relative calm olutside the shroud and on the top i.e. the contrast in Reynold Number profiles in different parts of the flotation machine. Such contrast must be characterised and then optimised to obtain best results.

Energetic considerations are important not only for the macro-level regarding aeration and agitation but also for the micro-level in terms of electrica double-layer interactions. S. Chander and D.W. Fuerstanau[21] have made a heroic, though unsuccessful attempt to explain the natural flotability of molybdenite kin terms of the concept of disjoining pressure $P = P_{vw} + P_e + P_h$ being negative for a gas-liquid-solid system where the three terms on the right hand side of the equation represent Vander Waal, electrical and hydration forces (pressures) respectively. P_h could not be accurately computed, bubble potential and solid surface potential at the edges could not be accurately measured, and theoretical objections persisted as to the computation of composite Hamaker Constants and their polar term counterparts. Irving Langmuir, the famous Nobel Laureate and surface scientist, was a minereal engineer in his early career, and wrote in 1920, that the newly discovered forth flotation process is very imperfectly understood. It was desired that after the passage of eight decades, we could make a more encouraging statement! However, we are firmly on the path of characterisation of our system and the journey must continue.

END PRODUCTS AND CONCLUSION

One should not forget to thoroughly characterise the end products. As a matter of fact, all the solid (and liquid) streams entering and leaving each section of the plant such as grinding unit, rougher, middling unit, regrind unit. cleaner etc. must be exhaustively and continuously (in an industrial plant) characterised.

In conclusion, it is emphasized on the two-fold rationale behind our strong prescription to characterise. How could anybody claim reproducibility of a set of data collected in an incompletely characterised system. The second argument now advanced after six years by the present author is even more profound. How could we *understand or quantitatively predict a phenonenon without characterising it ?*

There is nothing wrong in statistical modelling which is an useful approach in this age of computers. But this technique should be augmented with data on detailed characterisation as discussed in this paper. Very often modellers evade this task and hide themselves under mathematical complexity.

For example, froth flotation has been modelled as a first order kinetic phenomenon with its rate constant showing a distribution parameter. Very few researchers have correlated this distribution of k with the microproperties of the particulate system. In the case of sphalerite flotation system, why not isolate the slow and fast floating particles and determine their different sizes, shapes, adsorption magnitudes of collector and additives and surface compositions in terms of zinc and copper atoms, the latter being known to radically alter the flotability of sphalarite. Then the distribution of k could be better understood in terms of physics and chemistry and better articulated in terms of additional factors mathematically.

Alternatively, it would be left with the terse statement made by A. Broussaud[22] "The validity of a kinetic model is limited to the area in which factors governing the kinetics remain unchanged".

Unfortunately, there are many many factors which do not remain unchanged from one experiment to another. It is hoped that the basic researchers in mineral processing would transcend the useful area of black-box modelling and enter a new phase illumined by the myriads of basic characterisation data. Towards the achievement of reproducibility, basic understanding and predictability there is no other way.

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