PARTICLE SIZE EFFECTS IN THE FLOTATION OF CASSITERITE

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UNDERTAKING

I certify that this is my own work and has not been submitted for a Master of Science degree at any other University. The contract of th

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ABSTRACT

I I I I K E I I X I f l « f « f k « «

An investigation has been made of the effect that particle size has on the flotation recovery of cassiterite. This investigation arose because insufficient data existed about the flotation behaviour of cassiterite. This is because flotation of cassiterite on an industrial scale is a fairly recent innovation, although research along these lines has been pursued for the last forty years or so. Existing information on the floatability of fine cassiterite particle sizes, less than about $7 \mu m$, is limited, while most workers agree that the floutability of particles coarser than about 50 pm in size is very poor. Not much ia known about the floatability of fine particles because of the technique of desliming at about 7 pm which is carried out at all cassiterite flotation concentrators. This slime fraction is discarded.

Cassiterite samples from different localities were obtained for this investigation. Some of these samples were subsequently upgraded to a maximum practical degree of purity, viz. 94 to 98 per cent tin dioxide, while other samples with lower tin dioxide grades were also obtained. These samples were all thoroughly screened into size fractions. This was achieved by using Tyler screens and the Warman Cyclosizer. Some samples were subsaquently centrifuged to obtain fine particle size fractions.

Samples of 1 gram mass were used for the flotation tests. The sample was placed in the Fuerstenau Cell, a microflotation cell, and the required amount of collector, ethyl phenyl phosphonic acid, was added to the sample. The pH was adjusted to 5 with dilute sulphuric acid, and a conditioning time of 4 minutes allowed. Nitrogen gas was then introduced into the flotation cell for 3 minutes. The floated fraction was collected and weighed, as was the tailing fraction, and the recoveries calculated. Entrainment bahaviour, that is, recovery of sample by non-flotation

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means, was also determined for some samples. Pure flotation recoveries, as distinct from total flotation recoveries, were thus determined.

The effect of ultrasonic vibrations on cassiterite samples was also investigated. It was observed that cassiterite samples which had been subjected to ultrasonic treatment gave improved flotation recoveries compared wi-h samples which had not been treated. The effect that ultrasonics has on cassiterite was studied using a scanning electron microscope. The results obtained from this investigation has enabled a mechanism for this effect to be postulated. Thus, ultrafine material, generally smaller than $0,5$ μ m in size and comprising predominantly cassiterite, was found to adhere to the coarser particles. It is considered that these ultrafine particles are responsible for the inferior flotation results exhibited by the coarse particles.

It was found that cassiterite which had not been treated with ultrasonic vibrations, floated pocrly when compared with the flotation behaviour of galena. Also, cassiterite from different localities responded to differing extents when floated under identical conditions.

The recovery - particle size relationship profile for the pure flotation recovery of cassiterite was found to follow the expected pattern, that is, as the particle size decreased, the recovery increased to a maximum value, and then decreased again. The flotation behiviour of fine particles, smaller than 7 pm, was characterised in some detail.

It was found that the maximum recovery for the total flotation recovery of cassiterite occurred at about 10 to 20 pm. For pure flotation recovery, the maximum occurred at about 20 to 30 μ m, while the maximum recovery for pure flotation recovery of cassiterite samples which had been treated with ultrasonic vibrations was found to be at about 130 to 140 µm.

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1. INTRODUCTION

Historically, cassiterite, tin dioyide, has always been recovered by gravity techniques, whather it be a crude process like wind winnowing, as originally carried out at Brandberg West Tin Mine in South West Africa/Namibia at the turn of the century, or the more recently introduced Bartles-Mozley table (1). In the case of the Rartles-Mozley table, cassiterite may be upgraded by gravitational means down to about 7 µm in size, whereas normal shaking tables can recover cassiterite particles down to about 15 µm in size. Vanners, round frames and buddles can recover cassiterite down to about 10 pm in size (2). However, it should be noted that although cassiterite is recovered at these fine sizes mentioned, the recovery is very inefficient and only becomes acceptable for sizes coarser than those given above.

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Research work on the flotation of cassiterite was published as early as the 1930s, among this being investigatory work carried out at Renison Tin Mine (3, 4, 5). Apparently, research work to investigate the possibility of floating cassiterite industrially was started in the U.S.S.R. during the late 1930s (6). Extensive experimental work was done by Gaudin and co-workers (7, 8, 9, 10), as well as by Oberbillig and Frink (11). None of these ideas were put into practice.

The first commercial cassiterite flotation concentrator was started at Altenberg, Erzgebirge, Saxony, and operated during the period from 1937 to 1945 A mixed cassiteritewolframite ore, also containing other heavy metal minerals, was treated with oleic acid collector. Recoveries of about 77 per cent were obtained at concentrate grades of 11 to 12 per cent tin. However, no economic method existed during this period for the upgrading of these low grade concentrates, and the process could thus be considarrd only as a war-time expedient (4, 5).

Altenberg again featured in the ensuing developments regarding the flotation of cassiterite. The use of paratolyl arsonic acid was implemented at this concentrator during 1959 and this resulted in an overall increase in tin recovery of about 10 per cent and a slightly higher grade of concentrate (14 per cent tin). Despite the advantages of the new collector reagent, there were two important disadvantages which, together, ultimately led to the process being discontinued, viz. the reagent was very expensive and was toxic by virtue of the arsenic present (4, 12).

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The presence of ' rge tonnages of cisseminated finegrained cassiterite ore at Renison prompted the investigation of flotation during 1964, as a method of recovering the fine sizes not recovered by the gravity processes. A petroleum sulphonate was used as a collector, but results were disappointing. During 1967, a cullector SM119 (an organoarsenious compound) was made available from Japan where this reagent was being used at the Mikohata Mine for the recovery of cassiterite. Results wero sufficiently encouraging and led to the installation of a pilot plant, and subsequently a full-scale concentrator which was commissioned during 1970. Desliming was originally planned at a cut point of 2 μ m by using centrifuges, but this proved to be unsuccessful due to the unmanageable frothing which resulted. Currently, $desliming$ is being carried out at about $3 \mu m$ by using cyclones (3). At Renison, the gravity plant tailings constitute the flotation feed to the cassiterite circuit after sulphide mineral scavenging (13).

At this stage, it should be noted that it has long been realised that the desliming of flotation feed is imperative to the subsequent flotation of cassiterite. Although the effect of slimes on flotation is discussed in the following section, it should be briefly mentioned that fine particles adsorb excessive amounts of reagents, gangue

slime coatings prevent surface contact with the collector reagents and air-bubbles, and that recovery and grade are reduced because selectivity is reduced. Also, certain minerals have a greater tendency to slime, like chlorite, limonite and hematite, than other minerals (14). Because of these effects, desliming is carried out at all the cassiterite flotation concentrators. The desliming cut points may, however, vary from concentrator to concentrator.

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The investigation into the recovery by flotation of fine cassiterite from tailings dams at Union Tin Mine commenced during 1965 and a full-scale concentrator was commissioned during 1971. The test work a carried out for the Union concentrator was adopted at Rooiberg Tin Mine, and full-scale production commenced at Rooiberg in 1972. In both cases, cassiterite is currently being floated from the gravity concentration tailings as well as from old tailings dams. At both concentrators, desliming is carried out at a particle size of about $7 \mu m$ with respect to cassiterite. This desliming is ach aved by the use of several batteries of small high-pressure cy lones. The minus $7 \mu m$ material is discarded while the 7 to about 50 μ m particles constitute the flotation feed. Buncombe (15) described the desliming process at Union. The process is identical at Rooiberg. Sulphide minerals are removed by flotation prior to cassiterite flotation. At both Union and Rooiberg, sthyl phenyl phosphonic acid is used as the collector reagent $(3, 16, 17)$.

At the Wheal Jane Tin Mine, the concentrator was commissioned during 1971. A variety of cassiterite collectors were tested for this ore until a sulphosuccinamate was chosen as giving the best results. The desliming cut point for this concentrator is $7 \mu m$ (3).

In addition to the concentrator, referred to above, there are also five concentrators in Bolivia employing flotation for the recovering of cassiterite. However, no details are available about any of these concentrators except that they all deslime the flotation plant feed material at about 10 µm, and that Aerosol 22 is used as the collector reagent (IB).

Cassiterite is often very finely disseminated in the ore. This is the case at Union where the grain size of the cassiterite varies between 3 and 45 μ m (19). Other tin mines also have fine-grained cassiterite present in the ore, as at Rooiberg, Renison, Wheal Jane, and also the tin mines of Bolivia (3, 18). Fine grinding is thus necessary to liberate the cassiterite, and this results in the formation of slimes of both gangue and cassiterite. Cassiterite is very brittle and thus slimes easily.

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The introduction of flotation following the gravity concentration process at Union has resulted in an increase in the total recovery of tin from about 26 to about 46 per cent. At Rooiberg, the increase has been from about 74 to about 80 per cert. However, because of the desliming step, about 30 per cent of the tin in the potential feed to the flotation stage at the Union concentrator is lost (17). It has been determined that all the cassiterite in the deslime plant discard is less than 10 μ m in size, and that the great majority of the cassiterite particles are liberated (19). The value of the tin in the discarded slime is very substantial; it has been calculated to be worth more than one million rand per year at the Union Tin Mine alone for a prevailing tin price of R5 500 per tonne end a revenue of R2 500 per tonne (March 1974 values). The present revenue figure is not available.

It has been observed in practice that the presence of very fine particles is detrimental to the flotation of cassiterite particles between about *I* and 50 pm in size. However, since the minus 7 um cassiterite is discarded, it is not known what the flotation behaviour of this size material will be. Since a particle size and flotation recovery relationship for cassiterite has only previously beer, reported

by Kelsall et al (20) on material from Renison, it would be advantageous to study local cassiterite samples and de termine their flotation characteristics, especially for the particles smaller than $7 \mu m$. Also, as will be observed in a following section, there is reason to suspect that the upper particle size limit for the flotation of cassiterite, viz. approximately 50 μ m, is unexpectedly small. This dissertation has the objective of establishing the relation. ship between particle size and flotation recovery for cassiterite over a wide range of sizes so as to include the very small (less than $7 \mu m$) and the coarse (between about 50 and 350 μ m) particle sizes. Some practical implications will then subsequently become apparent.

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The approach to characterising the relationship between particle size and flotation recovery for cassiterite will be made employing a microflotation cell and cassiterite samples of varying grades from various localities each screened into different size fractions. The scanning electron microscope will also be used i order to elucidate certain phenomena observed or cassiterite samples which had been treated with ultrasonic vibrations.

2. LITFRATURE REVIFW

Since the following topics each form an integral part of this investigation, it was decided to review each in turn, viz.

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- (1) Cassiterite flotation
	- (2) The effect of particle size on flotation
- (3) The effect of slime coatings on flotation
	- (4) Ultrasonic vibration treatment

2.1 Cassiterite flotation

2.1.1 Fundamental studies

A brief look will now be made at some fundamental studies of cassiterite. These studies have been performed by many workers in an attempt to determine the conditions under which selective flotation of cassiterite could be achieved.

The point of zero charge (pzc), chat is, the pH value et which the solid surface will show no excess positive or negative charge, has been measured by various authors and appears to vary from 3,4 to 7,0 (21, 22, 73, 24, 25). Thus the cassiterite surface has the following configurations / $10H_2$, /SnOH and /SnO^t at pH values below, et, and above the pzc respectively (the symbol / represents the lattice surface schematically). This wide range of values for the pzc has been attributed to varying amounts of impurity elements present either as an isomorphcus substitution for tin, or else as impurity iors present in the cassiteritebearing gulps. This view is also held by Klessen and Mokrousov who regard the changes in flotation activity of a particular mineral in the presence of other minerals to be due to the presence of ions derived from these various other minerals. A number of workers have shown that the presence of foreign ions radically alters the flotation behaviour of cassiterite $(4, 11, 26, 27, 28)$. Thus, under varying conditions, ferric ions could act as a depressant, or as an activator for cassiterite. There exists an apparent conflict in the literature about ferric activation being necessary

or unnecessary in the flotation of cassiterite (29). Other metallic ions are generally considered to act predominantly as cassiterite depressants.

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2.1.2 Reagents used in the flotation of cassiterite In this section a brief look will be made at the various reagents which have been used in the flotation of cassiterite.

(1) Oleic acid and sodium oleate. A great deal of the early work on the flotation of cassiterite was carried out with oleate collectors. However, a major drawback with the use of oleate was the lack of selectivity of the reagent resulting in acceptable recoveries, but poor concentrate grades being obtained. The contaminating minerals were mainly iron oxides and hydroxides (4, 26, 29, 30).

(2) Succinic acid derivatives. The succinic acid derivatives have had a good deal of success in floating cassiterite. The best known reagent, Aernsol 22 (n-octadecyl te trasodium sulphosuccinamate), was found to be a good collector for cassiterite (31, 32). At present, this reagent is in use in cassiterite flotation concentrators in Bolivia (18). A succinamate collector is currently being used at Wheal Jane Tin Mine (3) .

(j) Alkyl sulphates. Reagents of this type have shown promise as a collector for cassiterite, but. as far as is known, no concentrator uses this typo of reagent. Experimental work $(27, 33, 34, 35, 36, 37)$ appears to indicate that the presence of iron markedly improved the flotation behaviour of cassiterite. However, Strel'tsyn (35, 38) reported that cassi erite could not be selectively floated from iron oxide minerals and tourmaline using alkyl sulphates.

' (4) Fetroleum sulphorates. Petroleum sulphonates were originally developed as a low cost flotation collector for iron-bearing minerals. Renison tested a reagent of this type during 1964 but found the collector to be insufficiently selective (3). These results were verified by Graham (39) using ore from Rooioerg. Wrobel (40), however, claimed selective flotation results using a sulphonate derivative.

(5) Arsonic, stibonic and phosphonic scid derivatives. Although paratolyl arsonic acid was the *f*irst reagent of this group to find practical application in the flotation of cassiterite, the toxicity of the reagent severely curtailed its use. Phosphonic acid derivatives have, and are being, successfully used at a number of concentrators, but the main inhibiting factor to its use is the excessively high cost of this reagent. This feature applies to the whole group of derivatives (3).

Kirchberg and Wottgen (14, 41, 42, 43) developed the phosphorus and antimony analogues of arsonic acid as new reagents for cassiterite flotation. The stibonic acid collectors were found to be ineffective and showed poor collecting properties, and work ceased on the use of this reagent, while the phosphonic acid derivatives gave promising results. In some cases the results of the phosphonic acid derivatives were superior to those obtained with arsonic acid collectors. It was subsequently datermined that the alkyl phosphonic acids were stronger and more selective collectors than the aryl phosphonic acid derivatives (4). Currently, phosphonic acid collectors ore being used at certain cassiterite concentrators, viz. Roniberg and Union Tin Mines, where ethyl phenyl phosphonic acid has replaced the paratolyl arsonic acid as the collector for cassiterite.

Results of comparisons between arsonic. and phosphonic acid collectors are conflicting, as is also the question as to whether iron activation is necessary (4, 30, 41, 44). Optimum pH range for flotation with phosphonic acid was ^ determined by Collins (4) tr be between 5,6 and 7,4, while Goold and Finkelstein (29) found this to be between about 4 and 6. Wottnen (45), however, found adsorption of collector to increase sharply at a pH of about 4 with the maximum being reached at a pH value of 2. These results by Wottgen are not easily explained when it is considered that the best flotation rr 'uits in practice are obtained at a pH of 5 as is curried out at both Rooiberg and Union Tin Mines.

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(6) Hydroxamic acid derivatives. Hydroxamic acid derivatives have apparently been successfully used as collectors for casnitorite in the U.5.5.R. Bogdanov et al (46) and Strel'tsyn (35, 38) reported good results in the flotation of gravity concentration slime, and also the upgrading of gravity concentration products. However, ironbearing minerals were detrimental to concentrate grade as these were also floated. Rosenbaum (47) considered the hydroxamic acid collectors to have the equivalent collecting power to the arsonic and phuephonic acid collectors, although these thoughts were not borne out by the results of Graham (39).
(7) Uther collectors. [rahar (48) floated cassiterite Trahar (48) floated cassiterite with alpha-sulphostearic acid, and a mi.ture of this acid and alpha-sulphopalmitic acid. The results showed these reagents to be superior to arsonic and phosphonic acid, Aerosol 22, sodium lauryl aulphonate and a hydroxamic acid derivative. No further work has been reported on this system. Marabini (49) studied salicylaldehyde reagents for the flotation of cassiterite. This reagent contains functional groups wnich have a specific affinity for the tin(4) ion.

¹ (8) epressants and modifying reagents. The most commonly used depressants in cassiterite flotation are sodium silicate and sodium fluoride which are added to disperse and depress gangue minerals respectively. However, sodium silicate should not be added in excessive amounts since it will then depress cassiterite as well, while sodium fluoride does not have any noticeable effect on cassiterite (50). Sodium fluorosilicate can be used to depress iron-bearing minerals, and can also act as a depressant for the silicate minerals (4, 46). Sodium 'luorosilicate is also claimed to depress fluorite, while other workers have found this reagent to depress tourmaline (35). Both these minerals are readily floated into the cassiterite concentrate when no modifier is present. Hydrofluoric acid and sodium sulphide are other reagents which have been used to improve the selectivity of cassiteiite flotation.

2.1.3 A discussion on a ssiterite

In the introductory section, cassiterite flotation practice has been briefly outlined. A short examination into the reason* why the flotation of cassiterite differs in many respects from that of other minerals will now be made.

(1) Cassiterite is chemically extremely inactive. Any attempts to modify the cassiterite surface usually lead to the modification of the surfaces of other minerals present, thus reducing selectivity.

(2) The surface of wetted cassiterite may be amphoteric. This may lead to inconsistent flotation results under apparently standard conditions. Thus it was found that samples of natural cassiterite differed quantitatively in their ability to be floated although qualitatively their behaviour was similar. Thus, under identical conditions, a collector reagent will float different natural cassiterite samples, but the total recoveries obtained will differ from sample to sample. This effect may result directly from the presence of other elements substituting for tin within the crystal lattice (see below) (33, 51).

() Isomorphous substitution by niobium, tantalum, iron, titanium, scandium, tungsten, manganese and zirconium for tin occurs readily under different geological environments. Alternatively, or idditionally, minute mineral inclusions of the above elements may be present within *a* cassiterite grain. Singh and Bean (52) reported the most prominent mineral inclusions in cassiterite to be tapiolite, tantalite, rutile, ilmenite, wolframite and magnetite. Similarly Osipova et al (53) also found a number of minerals occurring as microinclusions within cassiterite grains. Different surface properties of cassiterite may thus result (54, 55). In this regard, conflicting results were obtained in extensive work carried out by Pol'kin and his co-workers (6, 56, 57). They prepared synthetic cassiterite and doped this with a variaty of impurity elements. The changes in the floatabilities that resulted because of this substitution were ascribed to

variations in the lattice parameters which, in turn, affected the covalent nature of the sample, hence its hydrophobisity and, therefore, its reactivity with collectors. Although a number of workers have found pure synthetic cassiterite to respond very well during flotation with a variety of collectors $(26, 30, 33, 56, 57)$, Pol'kin et al (6) found the contrary with their synthetic samples. This appears to indicate that the nature of the samples of Pol'kin and his coworkers differed greatly from those of the other abovementioned workers.

(4) Cassiterite is Lsually an accessory mineral in lode and pegmatite deposits with low grades (generally less then 1 to perhaps 3 per cent). Many minerals having similar flotation responses to cassiterite are often associated with the cassiterite. This leads to low grade cassiterite concentrates on flotation uf these ores.

(5) The commercial flotation of other oxide minerals relies on a high feed grade and, since their unit value is low, the tailings value is not of critical importance. However, in the case cf cassiterite, even very low grade tailings have a significant value.

(6) Some cassiterites contain sulphur on their surfaces and could thus float naturally with frother alone, or behave like a sulphide mineral. This results in tin losses during the sulphide flotation step prior to cassiterite flotation (58). The problem of cassiterite losses in the sulphide flotation circuit immediately preceding the flotation of cassiterite, is known to occur at Rooiberg, Reniaon and Union Tin Mine concentrators (20). At Renison it was found that a high proportion of the cassiterite of plus 30 pm in size was floated in the sulphide circuit, where is cassiterite coarser than $40 \mu m$ was found not to float in the cassiterite circuit. This result could be due to the effect discussed above. The losses of ultrafine cassiterite during the sulphide flotation step, which precedes the cassiterite flotation step, and hence the

desliming stage, may in fact be due to the sulphide mineral particles acting as the carrier particles for the ultrafine cassiterite, that is, "piggy-back" flotation (59).

The above indicates the inherent difficulty in upgrading cassiterite by flotation.

2.2 The effect of particle size on flotation

2.2.1 Introduction

It has long been realised that particles of different sizes have different flotation characteristics. from tne very comprehensive review on the ' oatability of very fine particles published by Trahar and W.rren **x6C),** and by Jameson et al **(61),** it is apparent that this effect has perplexed many workers and it is only in more recent times that the information available from many observations and theories has been collated, and workable theses proposed.

2.2.2 Parti le size - recovery relationship Gaudin et al (62) made the first very detailed study of the relationship between particle size and flotation recovery. Their work was based on the analysis of the performance of operating concentrators treating lead, zinc and copper sulphide minerals. Their res its showed that the particle size - recovery curves are of asymmetric shape and that optimum recoveries are obtained in the size r-mge cetxveen 10 and 50 pm (60). The recovery falls sharply for particles arove 100 μ m in size, but only gradually for sizes below 10 μ m. This observation has been found to be consistent with namy subsequent observations made on a variety of diff rent minerals, although the size range for maximum !:•. ery dnon vary for different minerals and different cund. t nns. Trahar and W irren (60) compared nine different minerals and found the maximum recovery size range for each the these minerals under different conditions. In each unse it is apparent that the best flotation results are uttired in the intermediate particle size range which is a merally between 10 and 100 pm.

Trahar (63) determined that the batch flotation of galena was particle size dependent, and that maximum recoveries were obtained in an intermediate size fraction, while the coarse and fine size fractions both showed inferior results. Anthony et al (64) obtained similar results in the flotation of sphalerite. In both the above cases, it was found that each size fraction had **^t** ast and slow floating components so that the recovery increased over the time range chosen. The effect of increasing the flotation time was to extend the particle size range for maximum floatability towards the finer size end of the relationship.

2.2.3 Ihm effect of collector concentration In their work, Suwanasing and Salman (65) varied the collector concentration in determining the flotation characteristics of galena and quartz over a particle size range from about 300 to about 30 µm in site. In their study it was shuwn that the intermediate maximum floating size range can be extended to cover a wider particle size range by increasing the collector concentration. In the case of galena, the coarser particle size range was extended as the collector concentration was increased, while for quartz, both the coarse and the fine size limits of flotation were extended. From their results, it was apparent that the maximum floatability of galena took place in the size range between 40 and 70 μ m. This was determined by using barely sufficient amounts for one monolayer coverage of collector since this condition yields the greatest amount of information on the kinetics of the system. The maximum floatability for quartz appan I to be between about 50 pm and some value less than 3L pm which was the lower size limit of their investigation. The results of Suwanasing and Salman for galena are in good agreement with those obtained by a number of other workers $(66, 67, 68)$.

2.2.4 Tha scale of experimentation

Klassen and Mokrousov (66) found similar particle size recovery results to those obtained by Trahar and Warren (60).

However, Klassen and Mokrousov did determine major differences between laboratory tests and results from practice for the minerals galena and fluorite. They found the maximum floatability range to be substantially higher in the case of laboratory tests (60, 66).

Good correlation between operating concentrators and laboratory results were, however, obtained for sphalerite by Trahar and Warren (60), and the diffarencer mentioned above had apparently resulted because of different techniques and conditions.

2.2.5 The effect a bubble size

Klassen and Mokrousov (66) considered fine particles to be floated mainly by fine air bubbles precipitated from solution, while large air bubbles, formed by the coalescence of smaller bubbles, or bubble clusters, responsible for the flotation of very large particles. This statement implies that vacuum flotation conditions would enhance the flotation of very fine particles. These authors then present several results showing the advantage of vacuum flotation over normal flotation (69). Panu and Pandelescu (70) also found vacuum flotation to give improved results over normal flotation conditions for particle sizes smaller than 10 μ m. However, Meloy (71) is of the opinion that vacuum flotation is but a special case of normal, bubble attachment flotition, and has based this statement upon theoretical considerations of the flotation process. However, the explanations may lie in the fact that smaller bubbles are developed during vacuum flotation and that it is this feature, that is, small bubbles. whi .mproves the flotati n results. Jameson et al (61) coi ±dered that smaller bubble sizes and a greater number of bubbles would be beneficial to flotation. These authors also considered that the flotation of very fine particles would be greatly improved by the use of smaller bubble sizes. 2.2.6 fntrainment

Lynch et al (67) considered that there were two mechanisms for the transfer of particles from the pulp to the concen-

trate, viz. by flotation, that is, the adhesion of particles to air bubbles, and by entrainment in the froth, that is, recovery by non-flotation means. Their studies were made at a galena and sphalerite concentrator. In the galena circuit, selective attachment predominates for galena since natural galena has a hydrophobic surface and a high specific gravity. Sphalerite has a lower specific gravity than galena and is induced to float to a small extent only in this circuit. Thus the recovery of the coarse sizes of sphalerite (particle size larger than about 20 μ m) in the galena circuit is indicative of selective attachment, while the recovery of sizes finer than about 20 is characteristic of entrainment. In the case of non-sulphide qangue, the mechanism of transfer to the froth is entrainment. Thus, in the recovery of a particular mineral, the importance of either mechanism was found to depend on the nature of the mineral, the water recovery rate, the chemical flotation environment and the availability of air in the pulp.

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During the detailing of the relationship between particle size and recovery, Gaudin et al (62) observed the phenomenon of gangue entrainment. This was designated as "mechanical" carry-over of very fine particles into the froth product.

Although Trahar and Warren (60) recognised this flotation feature of entrainment and mentioned that flotation recovery by bubble attachment would be lower than that portrayed in particle size - recovery curves, no further discussion on this aspect is entered into, save that it is apparent that a decrease in concentrate grade would occur with decreasing particle size. Sutherland (72) and Jowett (73) both described gangue entrainment in terms of a simple physical model. A feature of this model is that the pulp dansity of the flotation feed greatly influences the extent of entrainment, while the feed rate also plays a role. Klassen and Tikhonov (74) considered the water recovery into the froth product to be the most important factor affecting the entrainment of gangue into the flotation concentrate.

Lynch et al (67) similarly found that ths rate of water recovery is related to the amount of gangue in the concentrate. In their flotation study of galena and quartz, Suwanas ing and Salman (65) also performed entrainment tests. In the case of galena, a graph was obtained with a maximum entrainment value at about 30 pm, decreasing towards both finer and coarser particle sizes. This effect has been ascribed by these authors to the native floatability that galena possesses by virtue of the presence of the element sulphur, which is extremely hydrophobic. Quartz showed a gradual increase in recovery with decreasing particle size. In this case the effect is due to mechanical entrainment since the surface of quartz is hydrophilic. This is due to the crystal structure of quartz which has strong ionic bonds, and the strong polar surface, which results on cleaving, attracts water dipoles.

In their recent review, Jameson et al (61) mentioned that few systematic investigations had been made. According tc these authors, there appear to be four ways by which entrainment may take place: (1) gangue in mineral grains, that is, unliberated grains, (2) entrainment of free gangue, (3) flotation of free gangue, and (4) slime coatings of minerals and bubbles with gangue. The relative contributions of each is not easy to assess. Work by other workers has shown that with hydrophilic minerals, the phenomenon cf entrainment cannot be eliminated in any flotation system. The drainage times in the froth were found to determine the extent of entrainment in a system to a large degree. Thus for deeper froths there appears to be greater selectivity due to the draining of the entraining gangue from the froth.

In their work, Gaudin et al (75) introduced the coefficient. of mineralisation to give an indication of the extent of flotation of the particular mineral being studied. The coefficient of mineralisation, M, for a pulp constituent is defined as the ratio between the concentration of that c onstituent in the froth product and its concentration in the pulp body. In their work with particles of very fine

sizes, they considered entrainment not to have taken place to any noticeable extent, since,by their definition,M would equal unity for entrainment, and all their results showed M to be greater than unity. Thus they considered their results to be due to flotation only. However, it could conceivably have been the case that both flotation and entrainment had occurred simultaneously which could have given M a value greater than unity. This eventuality does not seem to have been considered by these authors. This oversight appears even stranger when it is seen from their work that they obtained recovery results using no collector reagent, and found this to he due to entrainment since M was less than unity. This implies that entrainment hid, in fact, taken place in their system when collector reagent was present. From their results it is seen that the entrainment rate appears to reach a maximum at a particle size of about 2 pm, with the rate decreasing for both coarser and finer particle sizes. This appears to be in keeping with the results of Suwanasing and Salman (65) who also detected a decrease in recovery for the smallest particle size range investigated, viz. minus 37 pm. Conjecture could thus have it that the results of Gaudir et al (75) in the absence of collector represents native floatability (as postulated by Suwanasing and Salman) and not entrainment. However, it is equally important ta realise that entrainment will take place for very small particle sizes, and that this entrainment effect will increase with decreasing particle size. The difficulty with galena is that no easy distinction can be made oetween native floatability end entrainment, especially not under large-scale concentrator conditions.

2.2.7 Theories of the effect of particle size Although none of the theoretical models which are to be discussed in this section were applied in the thesis, it is felt that many of the underlying principles are of great value in view of the work done and the results obtained. It has thus been decided to incorporate a brief discussion of these models in the review.

It is "pparent that the flotation process is complex, and that it involves a number of principles which have not been fully characterised to date. Thus it is felt that theoretical models cannot represent the full process and are of somewhat limited value. However, these models will assist in obtaining a greater understanding of flotation.

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Thus the flotation process can be sub-divided into subprocesses which can he studied " ore simply, especially by studying the effects of changes made in any one of these subprocesses, for example, in particle size. The theoretical models assume the flotation process to comprise the following four steps, viz. (1) the introduction of feed material into the flotation cell, (2) the attachment of particles to bubbles, (3) the transportation of particles and bubbles from the oulp to the froth, and (4) the removal of the floated particles. Each of these steps can be further sub-divided to give a total of ten sub-processes. (see Table 1).

TABLE 1

The processes and sub-processes comprising flotation (60)

- (1) The introduction of feed materials
	- (i) Introduct on of pitp
	- (ii) introduction of air

- (2) The attachment of particles to bubbles
	- (iii) Collisions between particles and bubbles
		- (iv) Adhesion of particles to bubbles
			- (v) Detachment of particles from bubbles
- (3) The transport processes between pulp and froth
	- (vi) Transport of mineralised bubbles into froth
	- (vii) Direct entrainment of particles into froth
	- (viii) Return of particles from froth to pulp
- (4) The removal of flotation products
	- (ix) Removal of froth
	- (x) Removal of tailings

It is from an understanding withese sub-processes that basic flotation equations can be formulated. Two approaches have been proposed. One was put forward by those authors who have set up differential equations for (1) the rate of change of the total mass of particles in the pulp, (2) on bubbles in the pulp, (3) of particles in the froth, (4) on bubbles in the froth,and (5) of particles in the concentrate. The resulting set of five equations can only be solved by making a number of assumptions which provides a final flotation rate equation. However, this equition cannot be used to predict the effects of changes in particle size (60, 76, 77). It has been found that this approach does not provide any elucidation of the sub-processes which make up the flotation process.

In an alternative approach, as advocated by Sutherland (72) and Woodburr et al (78), the rate of flotation is considered to be equal to the product of three factors, viz. the rate of collision between particles and bubbles, the probability of adhesion, and the probability trat no detechment will subsequently occur. Analytical expressions for these factors were obtained and the final equation linked the rate of flotation to the particle size. However, assumptions made in this approach have limited the usefulness of this method, although it is easier to evaluate in terms of the sub-processes than the first approach.

The effect of particle size on each of the three factors will now be considered.

(1) The rate of collision. A comparison between theoretical results of the collision mechanism of Sutherland (72) and practical results as obtained from concentrators, show large discrepancies. This led to modifications being made by other authors like Reay and Ratcliff (79) and Flint and Howarth (80). Comparison of these three theories reveals that the collision rate decreases with particle size (Sutherland, and Flint and Howarth) while for Reay and Ratcliff the collision rate decreases to sizes of about $0,6$ μ m, after which it increases again since, as the size of the particles decrease, so the particles, under the influence of Brownian motion, diffuse and are captured by a bubble more rapidly. Thus under conditions of Brownian diffusion, the collision rate decreases with

increasing particle size until the hydrodynamic forces become predominant, after which the collision rate increases. A minimum in the collision rate is thus obtained at sizes of about $0,6$ $~\mu$ m. However, some of the assumptions made by these authors were over-simplified and this led to errors in the predicted collision rate calculations. Some of these assumptions were corrected by Collins, and the corrected collision rates are shown to result in a minimum at about 0,6 pm as before, but the magnitude of the collision rate has been increased (61).

Derjaguin and Dukhin (61) developed a theory for the collision of very fine pacticles which predicted that below a certain critical size, bubble-particle attachment ceased. This critical size has not yet been calculated due to the complexity of the equations involved. Meloy (71) interpreted the theory of Derjaguin and Dukhin as predicting that i 11 particles less than 10 μ m in size would be equally floatable.

Levich (82) developed a theory which predicted that ultrafine particles have a finite and constant collision rate with bubbles as the particle size decreased. Gaudin (83), in his theory, found that the collision rate decreases with decreasing particle size.

It is significant that most of the collision theories predict a decrease in the collision rate with decreasing particle size, although experimental verification in the very fine particle size range is lacking.

(2) The probability of adhesion. Bubble-particle adhesion depends on some physical and chemical mechanisms which will now be briefly considered. The induction time, that is, the period required to rupture the thin film separating the particle and the bubble and to establish contact, was shown by Sutherland (72) to be independent of particle size, but this was contradicted by Klassen and Mokrousov (84) who showed that larger particles required longer periods of time to establish contact with bubbles than smaller particles. This contradiction has rot yet been resolved.

Philippoff (85) calculated that the equilibrium contact angles decreased and that the dynamic contact angle ircreased with decreasing particle size. Philippoff concluded that this effect contributed to the poor flotation characteristics of ultrafine particles.

The momentum of a particle could play a significant role in that a finer particle has a lower momentum than a coarser particle. This could reduce the probability of attachment of smaller particles to a bubble (59, 86).

The rate of adsorption of reagents onto mineral surfaces may be dependent on particle size. Thus smaller particles may have increased rates of reagent adsorption if the rate controlling step is diffusion.

It was considered by Gaudin and Malozemoff (87) that fine particles had different surfaces to coarser particles, that is, the surfa es of the fine particles may have altered chemically due to the presence of soluble species in the pulp. However, Gaudin (88) subsequently discarded this view.

It has been claimed that the high surface energy of slimes is detrimental to flotation because it introduces a number of harmful effects into the system. These effects are increased solubility, increased hydration, rapid surface reactions and non-specific adsorption of reagents (59, 89). It is also of interest to note that for perfect crystals, the interfacial free energy per unit area does not vary with particle size. However, since most particles are not perfect crystals, the free energy could change with particla size, especially on grinding when stresses are introduced into the crystal lattice and the solubility may bn increased. Collins and Head (59) considered slime particles to possess high surface energies due to having been subjected to longer p .riods of grinding and milling. However, Trahar and Warren (60) considered that large particles may have more high energy sites than small particles since large particles have been subjected to impacts which did not result in breakage occurring. It has been determined that the interfacial energy per unit mass increases with decreasing size to such an extent that particles of about $0,1$ μ m will

start exhibiting significantly increased solubilities. Thus for normal flotation pulps containing slow-floating slime in the size range $0,5$ to $10 \mu m$, the solubility will not differ significantly from the larger and more readily floatable par ticles (60).

Regarding the extent of adsorption of reagent by different particle sizes, it seems that slime particles require a greater surface coverage of reagent for the same floatability than larger particles. This has been interpreted by Trahar and Warren (60) as indicating that ultrafines do not have more active surfaces than larger particles, and that the decrease in flotation recovery for the finer sizes cannot be attributed to differences in surface energy.

(3) The rate of detechrent. The balance of the adhesive force of a particle attached to a bubble over the disruptive force associated with the weight of the particle dictates the maximum particle size floatacle (90). It was thus concluded by Morris (91) that **decreasing** particle sizes would mean stronger net adhesion of the particle to the bubble. Gaudin (90) reached the same conclusion.

2.2.8 The effect of particle size on the flotation recover, of cassiterite

As has been mentinned in the introductory section, only one reference cou d the obtained where the effect of particle size on the flotation recovery of cassiterite was fully characterised, although several references ware found which mentioned some facts pertinent to this topic.

The full particle size - recovery relationship was determined by Kelsall et al (20). These authors found that recoveries in excess of 75 per cent were obtained between tne sizes $1,5$ and $20 \mu m$, with the recovery de reasing sharply for sizes coarser than 20 μ m (maximum floated size was about 44 μ m), and the recovery appearing tn decrease for sizes finer tnan 1,5 μ m, although no data was obtained for sizes finer than 1.5 μ m. The maximum recovery was obtained at about 9 μ m. Zambrana et el (18) mention that high recoveries are obtained

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at Bolivian cassiterite conrentrators, using Aerosol 22 as the collector reagent, in the size range 10 to 74 μ m, with recoveries decreasing by about 90 per cent above and below these limits. It is of interest to note that this reagent has been reported as floating cassiterite up to sizes of $200 \mu m (32)$.

A number of authors have found that arsonic and phosphonic acid collectors do not float coarse cassiterite particles. Thus Collins et al (92) found the upper size limit for cal Scrite to be about 45 μ m. Topfer (93) obtained very poor rect eries with particles coarser thin 40 um in size. Kirchberg (41) obtained a vary interesting comparison on the effect of particle size un the recovery of cassiterite using oleic acid and ersonic ecid collector reagents. With cleic acid, the best recoveries were obtained in the size range 45 to 100 um, while particles up t 200 pm showed reasonable recoveries. For irsonic acid, the best recoveries were obtained between 45 and 65 μ m, while the recovery of 200 μ m particles was negl gible. Moncrieff et al (3) mentioned that cassiterite particles coarser than 43 pm were very difficult to float. Juy and Kirkup (14) found optimum results in the size range between 15 and 54 µm using phosphonic acid as collector. Satisfactory results were obtained down to about 5μ m, while particles coarser than 54 μ m florted very poorly.

Recently, Granam and Frankel (94) found the maximum recovery to occur at about 13 pm for the Rooiberg concentrator. Recovery decreased for coarser and finer particle sizes. The particle size - recovery relationship at the Union concentrator was determined by de Ruijter (95). In this case it was found that the maximum recovery occurred at a particle size of about 8 to 10 pm, with recovery decreasing for coarser and finer particle sizes.

2.2.9 Conclusion

In conclusion, it appears that coarse particles of many minerals, that is, particles larger than about $\theta0$ μ m in size, are reasonably amenable to flotation recovery with the tenacity of the bubble-particle adhesion being the factor limiting the

upper size.

However, for the very fine particles, less than about 10μ m in size, a completely different situation exists. The factors influencing the recovery of these small particles have been discussed and it is considered by most authors that the flotation recovery decreases with decreasing particle size .

2.3 The effect of slime coatings on 'lotation Slimes are generally considered to be that fraction o' the ore which is too fine to be commercially exploited by the process developed for the coarser size fractions of that ore. Thus slimes vary in size according to the partic lar lene iciation process employed, but in the flotation process generally start their deleterious effects in the size range from about E10 µm and smaller (59). The most deleterious effects during flotation are generally the sht to be caused by low particle momentum, slime coatings and high reagent consumption resulting in lower flotation rates, lower recoveries, and lower grade of concentrate. These effects have been discussed in the previous section. The deleterious effects on the flotation process, as mentioned above, have been observed by a large number of workers, among them Evans et al (2)). Klassen and Tikhonov (74), Neczaj-Hruzewicz and co-workers (98, 57, 98). Nedogovorov (99), Fuerstenau et al (100), Arafa et al (101), Hemminqs (102)and Iwasaki et al (103).

fine particles originate in two w ys, that is, primary slimes which result from weathering and decomposition of the rock components, and secondary slimes which are formed during the comminution of the ore. There is nothing that can be done about the presence primary slimes since this is governed by the geological history of the ore deposit. The quantit; of secondary slimes depends on the liburation size and the natural breakage characteristics of the ore. Secondary slime formation can be minimised by correct usage of mill and classification circuits. This would imply a thorough rtudy of the mineralogy, and good process design,
It has been determined that certain minerals slime much more readily than others during the comminution process. Among these minerals that slime readily arc chlorite, sericite (fine-grained mica) and the iron-bearing minerals limonite, goethite, hematite and aiderite. The presence of these minerals in flotation pulps are often responsible for decreased floatabilities of normally floatable minerals (14, 58, 100, 103, 104). Another two minerals which have been + ound to prevent the normal flotation of other minerals are calrite and valleriite. Calcite has been observed to frrm slime coatings on sulphur thereby decreasing its floatability (96). The mineral valleriite is responsible for coating readily floatable copper sulphide minerals and preventing bubble-particle adhesion. These copper sulphide minerals, viz. chalcopyrite. chalcocite, bornite and cubanite, are ell readily floated when valleriite is not present (105).

In contrast to the above findings that slime coatings prevent bubble-particle attachment, is the work of Warren '106) who showed that the floatability of coarser scheelite particles (10 ^o pr) was not idversely affected by a coating of ultrifind \ldots . .3 than 1 μ m) scheelite particles. His investigations showed that these coatings resulted from non-electrostatic forces and occurred when the particles and the ultrafines had similar charges. The extent of the coatings formed were found to be dependent on the pulp density and the particle size distribution, and also the intensity of agitation. It was also found that slime coatings were easier to form than flocs of ultrafine scheelite under the same conditions.

The adhesion of fine slime particles to coarser particles was orig nally thought to be due to chemical interaction (66, 107, 108). It was considered that the formation of an insoluble, chemically formed, slime coating on the now altered surface of the mineral prevented flotation from occurring. This chemical theory has been shown to be unacceptable since many contradictory cases have been found, among them the work of Dorenfeld (109) who showed the slime coatings to be nonstationary in many cases.

Backoff (110) and Sun (111) postulated that the conditions controlling flocculation of mineral particles are the same as those that control slime coatings. An ionic hypothesis was proposed whereby it was considered that slime coatings were controlled by the sign of the ionic charges of both particles and slimes. Mutual attraction induced slime coating formation, whereas repulsion prevented slime coatings from forming. Essentially this hypothesis is supported by the work of Fuerstenau et al (100) and Arafe et al (101).

Klassen's plan (89) best summarises the various aspects of the slime problem in flotation, although it should be app reciated that not ell these ef fects may be manifested together in a particular flotation system.

2.4 Ultrasonic treatment As has been mentioned in the introductor, section, the technique of ultrasonic treatment will be employed in order to elucidate certain phenomena. A brief discussion of ultrasonics will now be given.

Ultrasonic vibration treatment is emerging as a field of growing interest in a number of ore-beneficiation processes because of the specif.c phenomena accompanying ultrasonic treatment. The main phenomena associated with ultrasonics are the cavitational field, and the physical, physico-chemical and chemical processes which occur within the liquid medium and, more particularly, at the phase boundaries in heterogeneous systems.

Ultrasonic cavitation predominantly determines the effectiveness of the ultrasonic action occurring within a liquid medium. The intensity of the cavitation determines the dispursal of solids in ultrasonic fields, surface film removal, ultrasonic etching, destruction of coatings of flotation reagents on mineral surfaces, as well as other technological processes. The ultrasonic cavitation process is controllable and this results in a very wide fir i of application of ultrasonics for hydrometallurgical processes. In the cavitational field there are intensive microturbulent pulsations in the thin layers of

liquid which are in direct contact with the solid particles, the forward propulsion of gases and liquids within the porous spaces of the solids in suspension which leads to dispersion, the exfoliation of the surfice layer, of the solid particles, a localised temperature increase (by reveral lundred of degrees Celsius), and an increase in pressure (by many thousands of Kilopascals). Additionally, under the action of the cavitational field, new active chemical products appear in the liquid while the properties of the liquid are altered, that is, the physico-chamical properties of water which is subjected to ultrasonic vibrations are altered slightly with respect to electrical conductivity, alkalinity and surface tension for example. The surface properties of the solid particles are also altered, for example by the migration of point and line defects within the crystal lattice towards the surface of the particle resulting in an increase in surface free energy, and a result int higher reactivity. These effects result in increased interaction between the solid particles and the liquid. Generally, the effectiveness of the ultrasonic influence is proportional to its strength (112, 113).

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The specific uses of ultrasonics in mineral processing are briefly,

(1) Destruction of adsorbed layers of reagents. The effectivaness of destruction of adsorbed layers of reagents by ultrasonics varies for different minerals and depends on the chemical composition of these layers, the density, the duration of treatment, the particle size, as well as other factors. The dest uction of adsorbed layers has been demonstrated in experimental work in the U.S.S.R. but it is not known whether this has been implemented on an industrial scale. The ultrasonic action on flotation concentrates of sulphide minerals in the presence of their respective collector reagents leads to certain minerals losing their flotation activity to varying extents, while certain minerals retain this activity. This is due to the destruction and removul of the collector from their surfaces. Thus galena lo3es its activity after a short treatment time, while chalcepyrite

retains its activity. Other minerals may partially lose their flotation activities. Ultrasonics have also been **applied to accelerate the breaking up of flotation concentrate** froths in the **J.5.S.R.** (112, 114).

(2) Alteration of mineral surface properties before heneficiation. The alteration of surface properties of particles by ultrasonic treatment has led to increased selectivity in flotation, and electrostatic and magnetic separations of minerals. For example, the ultrasonic treatment of slurries of zircon and ilmenite results in changes in the electrical resistivi iss of these miner is. the resistivity of zircon being increased (due to the removal of ferrous and manganiferous coatings which are good conductors, from the zircon surfaces), while the resistivity of ilmenite is reduced (due to the removal 3 a friable, porous, non-conducting surface film containing clay components). The removal of layers of this nature also results in a decrease of the amount of fines in the subsequent treatment circuit, and, also, more mineral surface is exposed to the action of the collector thus leading to an improvement in flotation conditions.

(3) Emulsification **n** flattion reagents. Emulsions **of water insoluble flotation reagents are often preferred as this may reduce the amount of reagent, required, and may also facilitate the introduction of difficultly soluble collector reagent into the flotation circuit. The use of ultrasonics in this field aids in obtaining stable emulsions without special stabilising reagents being present in the system as well**

(4) Increasing secondary concentration in the froth. Stoev and *atsen (115) have enriched the froth product obtained in the flotation of coal-quartz mixtures. Ultrasonic vibrations applied to the froth have led to an intensification of the secondary concentration effect in the froth.

It has been claimed by some workers that the use of water subjected to ultrasonic vibration before flotation enhances the recovery of some minerals, for example, chalcopyrite, limonite and jarosite, while reducing the recovery of other minerals like molybdenite and quartz. This is ascribed to

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ultrasonic treatment altering the properties of water as discussed previously (116). The change in the interaction which results between sonified water and the surface of the mineral will also effect the mineral particle attachment to an air bubble. A change in the frothing behaviour in sonified water was also detected due to the changes which occur during the ultrasonic treatment.

The effect of ultrasonic vibration on pulps immediately before flotation **is** to increase recoveries for some **minerals** like chalcopyrite and pyrite for example, while decreasing recoveries for other minerals like quertz and molybdenite. This is ascribed to surface oxidation of the mineral particles occurring during the ultrasonic treatment step, and the subsequent increased 'or decreased) recoveries re then due to the collector being able to adsorb onto the oxidised surface more readily (or less readily) (117). Other authors claim that the floatability is improved because of enhanced selectivity because of the larger number of active centres which have formed, that the amount of middlings which have to be recycled is reduced, and that the imputity content of the concentrates is reduced (113).

It appears that most of the work dealing with ultrasonic treatment and uses the reof h a been performed in the U.S.S.R. Although extremely encouraging results have been presented by the various authors, the process has apparently found only one industrial applic tion in the Western World, viz. in Israel at the Dead Sea brine mineral rec very works where ultrasonics is employed in the conditioning stage to hasten the adsorption of collector onto the desired mineral surface (118). However, it is app rent that ultrasonic treatment in

mineral processing has a very encouraging future because of the properties of the process which have been briefly dealt with in this section.

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3. EXPERIMENTAL

3.1 Sample preparation

A number of cassiterite samples of different grades were obtained from various tin minss. These samples were all individually treated so as to obtain some pure cassiterite samples, and some samples with varying grades of tin.
A gangue sample was obtained for purposes of comparison with the cassiterite samples, that is, in order to ascertain how gangue would be expected to behave in the cassiterite flotation circuit. A galena sample was also obtained in
order that the flotation behaviour of galena could be compared with that of cossiterite. The treatment methods omployed
for each sample are given in Table 2. (see overleaf).

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Explanatory notes

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T : The sample was screened dry using Tyler screens, and these size fractions subsequently tabled on a laboratory-size shaking table in order to upgrade the simple.

fa

MS : The samples were subjected to magnetic separation using a Frantz Isodynamic Magnetic Separator to remove the minerals **hematite, magnetite and siderite, and also any tramp iron** which may have been present. This step also results in a **small degree of upgrading.**

5 : The samples were screened dry, and subsequently screened wet, using Tyler screens. The smallest particle size fraction obtained this way was a minus 500 mesh fraction (less than 25 μ m).

555 : The minus 500 mesh particle size fraction was treated in a Warman Cyclosizer which provided six sub-sieve size **fractions.**

CS : The cyclosizer undersize was collected and subsequently centrifuged to obtain further size fractions. **The very small particle sizes were ootained by repeatedly** milling small samples of cassiterite in a Siebtechnik mill until adequate amounts of sample were obtained. In the case **of the Rooiberg sample, much more milling was done than for the other centrifuged samples and thus the very fins particle** size fraction CTR3 (smaller than 0,2 μ m) was obtained. The centrifuging operation was in each case repeated several times in order to ensure that a clean cut point was obtained. **The calculation to determine the cut point sizes for the** centrifuging operation is given in Appendix 1. DS : The samples were screened dry only using Tyler screens. ZZS : The minus 500 mesh particle size fraction was sized dry at 2 µm using an Alpine Multi-Plex Laboratory Zig-Zag **Classifier.**

The galena samples were kept dry throughout the sizing procedure to minimise surface oxidation.

A microscopic examination of the 2 to 25 um galena size fraction showed that the separation at 2 µm was not vr.ry efficient since a not negligible amount of particles smaller than 2 um was also present in this sample.

All the particle size fractions for the various samples used in the investigation are given in the Tables .Al to All in Appendix 2.

3.2 Equipment

Since only gram-quantities of samples were available for characterising the relationship between particle size and recovery, the use of a micro-flotation cell became essential.

Initially, the Partridge and Smith (119) microflotation cell was employed. The reason for having chosen this cell was because no frother was required for any flotation tests and possible frother-mineral interactions would not be introduced into the system. However, the use of this cell was discontinued when it became apparent that unacceptably large entrainment values were being obtained.

The Fuerstenau micro-flotation cell (120) was then chosen for the study. The Fuerstenau cell is shown in Flate 1. The cell is 96 mm high and 55 mm in diameter. The depth between the sintered-glass disc and the froth lip is 56 mm. The froth lip on the rim of the cell facilitates I'm th removal. The sintered-glass disc of porosity number 4 acts as a gas diffuser. Nitrogen was used throughout cs the gas phase. A variable speed mechanical glass stirrer was used to agitate the suspension.

The ultrasonic treatment of the samples was performed using a Bandelin Ele tronic KG Sonorex G7120 vibration generator. The generator prodi ed a frequency of 35 kHz with an output intensity of 24DW. The ultrasonic cleaning bath was 250 mm in diameter and 150 mm deep.

The scanning electron microscope employed for studying certain ultrasonic effects was the instrument at the Council ror Scientific and Industrial Research (C.S.I.R.) at Pretoria. The instrument is the JEOL (Japanese Electron Optics Laboratory) J5M-U3. This instrument has the facility to perform chemical analyses of samples provided the elements are heavier than sodium. The analysis is performed by electron beam excitation.

3.3 Experimental technique

One gram samples were weighed out and placed into the Fuerstenau cell. Collector at the required initial concentration was then added to the cell. The collector solution volume used throughout was 70 ml, while the initial concentration of collector reagent was generally 500 mg/1. The collector reagent used for cass iterite flotation was ethyl phenyl phosphonic acid (EPPA). The sample was then conditioned for a period of 4 minutes during which the pH was adjusted by the addition *sf* dilute sulphuric acid to 5,0. Frother (Dowf roth 250) was added during the final minute of the conditioning period. In order to obtain the froth bed depth of about 15 mm which would be sufficient for the duration of the experiment, it was found empirically that an addition rate of 0,35 ml of a 6.7 g/l solution would be required. After the conditioning period, the gas, nitrogen, wis introduced into the slurry. An aeration rate of 500 ml/min, controlled by use of a rotameter, was found to give the optimum froth depth of about 15 mm.

The floated material was removed from the froth by scraping with a Perspex paddle onto the lip of the cell, and then into a container. The flotation μ iod was 3 minutes. At the end of the flotation period, the tailings were transferred to another container. The products were then dried and weighed, and the recovery calci ated simply as the mass of floated material divided by the total mass and expressed as a percentage. The temperature was controlled to between 22 and 23°C.

In order to investigate the relationship between particle size and flotation recovery of cassiterite, it was considered necessary to briefly study the following flotation variables.

(1) Conditioning time. Prior experimentation had shown that a substantial decrease in recovery occurred with increasing conditioning time, the most rapid decrease in recovery occurring during the initial 2 to 3 minutes of the

conditioning period. However, after a conditioning period of 4 minutes, the recovery - conditioning time relationship had stabilised. A conditioning period of 4 minutes was thus employed for all the c ssiterite flotation test work.

(2) Flotation time. The effect of flotation time on the recovery of cassiterite was studied. Figure *i* shows the results obtained for two different samples. From this it is observed that, of the cassiterite which floats, the flotation response is very rapid. This condition was also noticed by Goold and Finkelstein (29) who alsh floated cassiterite under similar conditions. Since flotati h is effectively completed after three minutes, it was decided that this period would serve as the flotation time. Although Figure 1 (part 2) gives th. flotation times at 2 and 4 minutes, and not at 3 minutes, it serves to illustrate the effect of flotation time on recovery.

(3) Initial concentration of collector. In common with other flotation systems, it was found that the recovery of cassiterite increased with increasing amounts of collector addition until a plateau was reached whereafter great increeses in collector additions resulted in only small increases in recovery. This is shown in Figure 2 (curve 1). This type of curve was noticed for the smaller particle size samples, that is, less than about 50 μ m in size For coarse particles (larger than 100µm), it is seen that an increase in collector addition had led to a proportional increase in recovery (see curve 2, Figure 2). In this case, the plateau had not yet been reached even sfter a collector addition of 2 000 mg/l EPPA. A discussion of the above effect for coarse particles will be given in a later section.

It was decided to perform all the experimental work at an initial concentration of 500 mg/1 EPPA since this represents an excess amount of collector with respect to coverage of the particles in monolayers for even the smallest particle size fraction investigated, viz. $0, 2$ μ m. (See Appendix 3 for the calculation) .

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Giher fictition conditions - Standard $37 - 25$ Hm 2 minutes Flotation time Paricle size Sample

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ther Flutation conditions - Standard $125 - 104$ μ m Rnoiberg
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The effect of initial collector concentration on the total concentration (mg/i EPPA) flotation recovery of cassiterite P. FIGURE

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At this stage it must also be pointed out that the recoveries shown in Figures 1 and 2 represent the total recovery and include some cassiterite recovered by entrainment. Thus the recovery due to entrainment is shown in Figure 2 hy the recovery obtained in the absence of collector reagent for the particular particle size. Although the recovery values should be corrected for entrainment (by deducting the entrainment value to obtain a pure flotation recovery value), it will be assumed at this stage that the entrainment values can be neglected since relatively coarse sizes were used and the entrainment values are therefore low. However, the whole matter of entrainment will be dealt with in greater detail in a subsequent section.

(4) pH. The pH of the flotation circuit at both the Rooiberg and Union concentrators is 5,0. In erder to confirm that this value is optimum for the microflotation scale performed here, the relationship between pH and flotation recovery was established. Figure 3 shows the relationship obtained. It can be seen that the maximum recovery obtained occurs at a pH value between 4 and 5. Goold and Finkelstein (29) obtained a similar relationship, the only difference being that their maximum recovery occurs at a pH value of 5,0. The present results indicate that a pH of 5,0 is in the region where maximum recovery occurs. This thus confirmed that a pH value of 5,0 will result in optimum recoveries being obtained. The different origins of the cassiterite samples used may be responsible for the small difference observed between the present results and those of Goold and Finkelstein.

(5) Temperature. The effect of temperature on the flotation recovery of cassiterite was briefly studied. The results are shown in Figure 4 where two sets of results are denicted. The results are unexpected and not well understood. It is considered by several cassiterite flotation concentrator metallurgists that higher pulp temperatures are beneficial to cassiterite recovery, although experimental data is lacking (16). However, since these results are not without interest,

Other Flotation conditions - Standard $m1 - 52 - 16$ Rodiberg 0.6 a Chrve 1 Sample weight Particie size **Cample**

Curve 2

Direr (lotation conditions - Standard 250 mg/1 EPPA $175 - 104 \mu m$ 2 minutes Rooiberg Initial collector concentration Flotation time Partitie size Semple

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it was decided to briefly describe them in this section.

As can be seen from the graph, the effect on the recovery for the fine particles is marked over a small temperaturs range, while for coarse particles the effect is minimal although apparently the trend is reversed. Because of these variations of recovery with temperature, the temperature was maintained closely between 22 and 23°C.

(6) Collector reagent EPPA. This reagent was supplied by Hoochst South Africa (Proprietary) Limited. EPPA is an anionic aliphatic phosphcnic acid derivative with the following chemical constitution,

> \sim \sim R - P \equiv 0 where R = ethyl \rightarrow $y1$ nu rau.cal

The reagent in the acid form is sparingly soluble in water. The sodium salt has a solubility to a concentration of 25 per cent in water. The procedure adopted to abtain EPPA in solution was to dissolve sodium h.droxide in distilled water, and then to add the solid EPPA. Subsequent stirring ensured dissolution. The solid EPPA, as well as weak solutions of up to 1 per cen* of EPPA are claimed to be very stable (121, 122). However, some erratic results were obtained with EPPA solutions which had been stored for various lengths of time, and thus fresh EPPA solutions were made up at the start of every batch of tests. EPPA was used throughout as the collector reagent for cassiterite.

(7) Galena flotation. The flotation technique for galena was similar to that employed for cassiterite, except for some variations which will now be described. The conditioning period employed was 3 minutes. The pH of the pulp was maintained at 9,0 using dilute sodium hydroxide. The volume of frother used was 0,4 ml per test at the concentration previously given. The collector reagent used for galena was sodium ethyl xanthate. The other conditions were all identical to those under which cassiterite was floated. Initially an excess of collector was used, that is, sufficient

collector for more than one monolayer coverage by the reagent, in keeping with the situation for caseiterite. However, it was only when starvation quantities of collector were used, that is, collector for only one .nonolayer coverage, that the recovery - particle size relationship for galena was determined. The results are shown in figure 11. Also shown in Figure 11 is the entrainment characteristic for galena. Initially no depressant was used in determining the entrainment for galena. However, the values obtained were erratic due to the natural floatability of galena which prevailed under these conditions. Potassium drchromate was then used as a depressant and the entrainment effect was then characterised. The depressant addition was found to have the optimum effect at 1 0U0 mg/2 initial concentre-ion (or higher).

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(8) Ultrasonic treatment. Samples of 5 g each were placed in six beakers each with a diameter of 40 mm containing 50 ml distilled water. These beakers were placed in the cleaning bath and, in ordur to protect the transducer, water was added to the bath to a depth of about 25 mm. The samples were then treated with ultrasonic vibrations for the desired length of time. The fine particles which were removed from the surfaces of the coarser particles were washed away with distilled water. The samples were then dried and stored.

All the results used in the graphs have been tabulated in Appendix 5.

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4. RESULTS

4.1 Reproducibility

Replicate tests were carried out on samples having different particle sizes in order to determine the reproducibility of the flotation procedure over the whole recovery range. The results of the tests carried out on the Rociberg samples are shown in Table 3. The variation of standard deviation. the coefficient of variation and the standard error with recovery are given in Table 3 at the 95 per cent confidence limits. This data is shown graphically in Figura 5.

From Table 3 it is apparent that the highest standard deviation obtained is 3.2 per cent, while the highest standard error is seen to be 1,5 per cent. It can, therefore, be expected that all the results will be better than, or equal to, these figures given above.

It is pheerved that the higher values of standard deviation and standard error tend to occur in the middle range of the recoveries, while the lower values tend to occur at the higher and lower recovery values. As will be seen at a later stage, the reason for this probably lies in the fact that the extreme recoveries have the least sensitive variations by virtue of their being in the stable areas of the relationship between particle size and recovery. The middle recovery range represents the area where the recovery rapidly increases as the particle size decreases.

Fuerstenau (120), who was the first to use a flotation cell of this nature, that is, the Fuerstenau cell, claimed to have obtained good reproducibility in the tests he had performed. However, with the actual results obtained by fuerstenau not being available, no further discussion about the reproducibility of his work can be given.

The reproducibility of this type of cell was found to be reasonably good at the National Institute for Metallurgy, Randburg. Thus willison and Finkelstein (123) obtained standard deviations varying between 1,8 per cant for recoveries between 90 and 108 per cent, and 11,5 per cent for recoveries between 20 and 30 per cent. All the other standard deviations lie

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between the values 4,2 and 9,8 per cent. It is apparent that the reproducibility results obtained during the course of this investigation are superior to those obtained by Allison and Finkelstein.

The furmulae used to calculate the statistical data is given in Appendix 4.

TABLE 3

Replicate tests carried out on Rooiberg cassiterite samples

Notes. 1. The Student t-distribution was used to establish the confidence limits since the sample distributions were small (124) .

2. Figure 5 does not represent the relationship between particle size and flotation recovery for cassiterite from Rooiberg, since in a number of cases the flotation conditions were not standard. These tests were performed solely to determine the reproducibility of the system over the whole recovery range.

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Mean recovery.

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4.2 Entrainment

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During the course of the experimentation, it was noticed that the finer particles tended to be recovered into the froth without any collector being present. Tests were thus performed in order to elucidate this effect. In the case of these entrainment tests, the conditions were identical to those used in the ncrmal flotation tests except that no collector reagent was introduced into the system. The results are given in Figures 6, 7, 8, 9, 10 and 11, together with the flotation recovery results. As is to be expected, the results for cassiter.te show that the smaller the particle size, the greater the extent of entrainment into the froth.

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Lynch et al (67) showed that the smaller the particle size of the gangue, the greater the entrainment that results. These authors also found that the extent of entrainment was also affected by the rate of water re , ered in the froth in any flotation system. For this reason, the water recovery was Lept constant for all the flotation tests performed during the couase of this investigation.

Suwanasing and Salman (65) studied entrainment of galena and quartz over a range of particle sizes from about 295 um to a minus 37 pm size fraction. For both minerals entrainment was observed th begin at about $178 \mu m$. In the case of galena, a maximum entrainment value was obtained at a parti-ly size of about 40 µm, the entrainment value then decreasing again for smaller sizes. With quartz, no such maximum was found and in this case the entrainment value increased with decreasing particle size.

The quarts entrainment results of Suwanasing and Salman (65) d *ffbr* from the gangue entrainment results obtained in this study (if a direct comparison be valid) in that the lacter results also show a maximum. This maximum occurs between about 10 and 15 μ m which represents smaller particle izes than those sed by Suwanasing and Selman. Also since the gangue sample prised a number of minerals, for example, quartz, aricite, feldspar, hematite, magnetite, pyrite, tourmalins, calcite and I jurits, it co Id he possible that agglomerate furmation had

occurred for the very fine particle sizes and that these agglomerates would then have behaved as much coarser particles. A further feature of the work uf Suwanasing and Salman is that The entrainment of quartz commences at a particle size of about 178 pm. In the present investigation, gangue entrainment appears to begin at about 80 μ m (see Figure 10). It can thus be seen that a direct comparison of the quartz sample of Suwanasing and Salman, and the gangue sample of this work, cannot be made because of the observed differences in behaviour.

The results of Suwanasing and Salman for galena are similar to those obtained in the present investigation in that the shape of the graph is identical, although the maxima are at different particle sizes. Thus Suwanasing and Salman obtained a maximum entrainment value at about 40 pm whereas, in this investigation, a maximum was obtained at about 15 pm (see : igure 11). Also, from the galena entrainment results of Suwanasing and Sulman, it appears that antrainment commences at about 178 um whereas, in this investigation, galena entrainment begins between about 40 to 50 μ m. The entrainment for cassiterite also commences between 40 and 50 µm.

Apart from the different flotation conditions which prevailed when the results were obtained, it is apparent that the differences in the results for galena were due to the fact that use was made of a known galena depressant, potassium dichromate, during the course of the present work, whereas t' is was not done by Suwanasing and Salman. Their results, therefore, suggest the property of native fInstability, which galena possesses, and that this is responsible fur an apparent entrainment response being obtained at such coarse particle sizes, whereas the results from this study show predominantly true entrainment results. It should be noted that erratic results were obtained for galena when entrainment determinations were attempted in the absence of a depressant.

The entrainment values obtained for cassiterite and gangue are compatible with their densities. Thus it would be expected that gangue (specific gravity less than 2,8) would have higher entrainment values than cassiterite (specific

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gravity 7,0) rar any particle size, and that galena would have the lowest values (specific gravity 7,9). This is, in act, the case for the coarser sizes. However, for the very fine sizes it appears that there are other factors which become important and these will be discussed in a subsequent section. It also appears that although the potassium dichromate depressed the tendency of galena to float naturally, it did not do so completely since some residual native fInstability seemed to remain.

Entrainment tests were also performed on a cassiterite sample from Rooiberg which had been subjected to ultrasonic treatment. The results are shown in Figure 24 which also presents the entrainment resu.ts of an identical sample from Rooiberg which had at been subjected to ultrasonic treatment. As can be seen, there is a significant difference in the entrainment values obtained. The discussion of these results is to be dealt with in a subsequent section.

t must be stressed, however, Lnat in this investigation all the entrainment values are given on the basis of a three minute flotation treatment period. It is apparent that when entrainment tests are being performed, periods longer than three minutes will result in higher entrainment values, and vice versa. This argument also holds for flotation tests since the longer the flotation period, the greater the extent of entrainment which will result since entrainment is a purely physical phenomenon, and pure flotation may already have ceased.

The distinction will henceforth be made as regards the total recovery, that is, the value which gives some idea as to what would take place in a real flotation system and will thus include entrainment, and pure flotation. that is, the aspect of particle-bubble collisions. Hence, pure flotation will be employed to mean the totel flotation recovery minus the entrainment value obtained.

It should also be stated at this stage that wherever particle sizes ore mentioned, it must be remembered that it is not any specific particle size but rather a median particle size that is being considered.

4.3 Perticle size

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The effect of particle size on the overall total recovery of cassi :erite in a flotation test was studied using the samples discussed in *a* previous section. A galena, and a gangue sample, was studied in a similar way. The galera sample will be discussed in a following section. The results for the cassiterite samples are shown in Figures 12, 13 and 14 (employing a logarithmic scale to accentuate the finer particle sizes) and Figures 15, 16 and 1? (employing a linear scale to accentuate the coarser particle sizes). Figure 18 gives the results as obtained from a detailed analysis o* the flotation material of the Union concentrator (95). These results are all tabulated in Appendix 5. It can be seen from the results at the Union concentrator that the maximum cassiterite recovery takes place at about 9 um if the recovery is calculated per size fraction, that is, the feed to the concentrator and the flotation concentrate and tailings are all sieved into size fractions and the recovery calculated on this basis. The maximum is seen to occur et about $10 \mu m$ if the recovery is based on the total feed to the flotation circuit, that is, in this case reporting the recovery as the cassiterite recovered in the concentrate which is sieved into size fractions, and the recovery from each fraction calculated as a percentage of the total feed.

The results for the Rooiberg concentrator are about 8 and 12 µm respectively (94). Kelsall et al (20) found the maximum recovery at the Renison concentrator to occur at about θ μ m. It is seen that the median particle sizes for maximum recoveries do not differ greatly according to these results obtained from detailed studies of ihe material from the above-mentioned concentrators. In fact, these sizes can, for practical purposes, be regarded as being virtually identical

since the entrainment effect is not being considered at this stage.

The maximum total recoveries for the various cessiterite and the gangue samples are given in Table 4.

However, there is more to these results than that which is immediately apparent. On accounting for the entrainment values obtained (for those samples where entrainment tests were performed), the pure flotation recovery values are obtained. These values are plotted on Figures 6, 7, 8, 9 and 10 for those samples where entrainment values were also determined. As can be seen from these results, the sizes for maximum recovery are displaced t wards coarser sizes, because, as has been seen, the entr inment increases regularly with decreasing particle size, the a resulting in the total flotation recovery being redurew more substantially for the finer wizes than for the coarter sizes whe e entrainment is almost negligible. The pure flotation secovery results obtained this way are given in Table 4.

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As combe seen from the repective graphs (Figures 12, 13 and .4) the Union. Romiberg gravity concentrate and Renison total recovery cur.es all show a minimum in the very fine particle size cange. while the curve for Rooiberg apparently has a minimum. The reason for this phenomenon is not immediately alear. However, some discussion will be entered into in a subsequent section.

It is also seen that there is some scatter in the values particularly for the Kamativi and Wheal Jane samples. In the case of the Wheal Jane samples, the scatter arose in the sizing procedure. Since it is a low grade concentrate, the cyclosizing process was responsible for imparting a density-particle size classification to the samples. Thus each mineral in the cyclosizer size fraction has a different particle size range. the low specific gravity minerals having much more coarser particle sizes then the high specific gravity minerals. The screening procedure does not have this effect on the samples. It can be seen that the discrepancy occurs where the screening of samples stopped, and cyclosizing of samples began, that is,

between 20 and 40um. In the case of Kama vi, no direct answer can be found to explain the observed scatter sines repeated work presented identical results. The scatter of these samples must be considered as having arisen from the experimental procedure.

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TABLE 4

Median particle sizes for maximus total flotation recoverius, and pure flotation recoveries

4.4 Cassiterite from different logalities

As has been discussed before, natural casalterite has a tendency to contain minor to appreciable amounts of substitution elements. The presence of either these substitution elements, or any mineral inclusions, may affect the flotation characteristics of the particular cassitarite. It has been claimed by a number of puthors that the presence of iron affacts the flotation of cassiterite. Yet other authors again consider the degree of crystallinity to be responsible for the differences in the results reported for various cassiterites. These aspects have been discussed in a previous section. In view of these conflicting views, it was thought that this investigotion, which was to study the flotation behaviour of cassitarite samples from different localities, could possibly provide new. information on these aspects. Table 2 mives the origin of the samples used as well as their respective tin and iron analyses.

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From the recovery-particle size relationships obtained, it can be seen that the approximate order of flotation response is Wheal Jane < Union < Renison < Rootherg gravity concentrate \approx Roofberg < Uis \approx Komativia Zaniplaats. This response is particularly noticeable in the flotation of coarse particles larger than 100 um in size (see Figures 15, 16 and 17, and Appendix 5 for flotation results). The linear graphs show up these differences best. This observed order in the flotation response is perhaps not unexpected when comparing the tin analyses of the samples. However, the Union result appears to be out of place when employing this criterion.

It is also of interest to determine whether the presence of iron could be responsible for the observed differences in flotation response. From Table 2 it is seen that the lowest iron values are associated with the cassiterite samples which have the best response to flotation, although this cannot be regarded as a definite rule since the iron in the Union sample is relatively low and yet the flotation response is not so good ralative to that of Rnoiberg or Uis, for example. Also it should be noted that with the lower grode cassiterits samples, the iron value represents the iron in the bulk of the sample, and not

necessarily the iron present within, or associated with, a grain of cassiterite. It is thus apparent that no definite conclusion can be reached about the presence of iron and the effect it has on the flotation of cassiterite.

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Since there exists this difference in the flotation response for the different samples, it was decided to test each sample to determine the degree of crystallinity and thus determine whether or not this factor could be responsible. Thus a sample of each of the cassiterite samples in Table 2 was submitted for X-ray diffractometry. A particle size Traction between 25 and 37 um was used for each sample except Wheal Jane where a 37 to 43 im sample was used. The diffraction patterns obtained for each sample were very sharp, and no broad La us indicative of lesser degrees of crystallinity were observed for any of the samples. Hence variations in crystallinity did apparently not effect the flotation responses.

Some of the cassiterite samples were subsequently submitted for spectrographic analysis in an attempt to determine whather there existed any chemical differences in these samples which could explain the different flotation responses observed during experimentation. The details are given in Table 5.

TABLE 5

Explanation : M - Major constituent m Minor constituent $m -$ - Low minor constituent - Trace constituent Higher trace constituent 1- - Lower trace constituent nd – Not detected 1 1 **+**

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Notes : . . Two Romiberg samples were submitted. One of these samples had been treated with ultrasonic vibrations, while the other had not been treated. No effective difference was observed between the two samples.

2. The fact that the Renison sample shows a significantly lower iron analysis than the other samples is contrary to the chemical analyses performed (see Table 2). This *x* isult is a cuntraliction and cannot be explained.

Gr entontein Tin Mines, Transvaal, RSA, were included in this analysis in order to obtain more complete data of the constitution of cassiterite from different localities. Thus overall, it can be seen that the major impurities in the various cassiterites are iron, silicon, magnesium, aluminium, and in one case manganese, while there are a large number of elements present as trace impurities. Cassiterite from Rooiberg "C" and

From the spectrographic results in Table 5 it is seen that there appears to be nu link ba ween the element impurities and *he different fl tation responses observed. Also significant is the fact that tantalum, niobium and tungsten were not detected in any of the samples. These three elements, together with iron, have an apparently favourable effect on cassiterite flotation according to $F \circ l'$ in et al (6) , and are commonly found substituting for tin in cassiterite. Also, according to the work of Pol'kin et al.manganese and copper have a deleterious effect on the floatability of cassiterite. However, in this work, copper is present in all the samples in about an equal amount, and the flotation responses have been found to differ. In the case of manganese, the best flotation results were obte: .ed with cassiterite containing this element (Union cassiterite also has manganese pres.nt), whereas the other samples did not have manganese. However, according to Pol'kin et al, the presence of manganese is detrimental to the floatability of a cassitelite

containing this element. It is apparent that the effect of impurity elements within the cassiterite lattice cannot be explained as simply as Pol'kin et al (6) have attempted to do in their work.

Pryor and wrobel (54) classified cassiterites from different ore deposits into three broad groups, viz. cassiterite from (1) pegmatite deposits, (2) from quartz and quartz-feldspar veins and (3) from sulphide deposits. Using this broad classification, it is found that Kamativi, Uis and Zaaiplaats are pegmatite deposits. Wheal Jane, Union and Rooiberg belong to the quartz and quartz-feldspar groups, while Renison is classified as a sulphide deposit (125, 120, 127). Hence, it could be surmised that the geological history and character of the deposit may have an influence on the flotation behaviour of the cassiterite. This then is the only link which can be found to explain why the cassiterite from Uis, Zaaiplaats and Kamativi floats better than the cassiterite rrom Rooiberg, Renison and Union. The Wheal Jane sample is not considered be_{-ause} of the low grade of the sample investigated.

4.5 Galena flotation

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It was considered that a comparison of the recovery-particle size relationship, as obtained for cassiterite, should be made with a sulphide mineral which has this relationship already elucidated. Galena was chosen for this comparison. The flotation of sulphide minerals, and in particular galena, has been characterised more filly and is better understood than oxide flotation. Gaudin et al (62), Klassen and Mokrousov (66) and Traher and Warren (60) have, amongst others, presented results characterising the recovery-particle. **size** relationships of sulphide minerals.

Thus galena samples of varying particle sizes ware floated in the same way as the cassiterite samples, except for small differences in technique. The results of the effect of particle size on the flotation recovery are presented in figure 11 for varying initial concentrations of collector. The entrainment results are also presented in Figure 11.

From the entrainment results presented in Figure 11, it is believed that the property of native floatability of the galena could not be suppressed entirely even though a high concentration of galena depressant was added to the system. This belief is based on the results which show that the entrainment values do not continue to increase with decreasing particle size, as do the cassiterite samples. Thus the entrainment curve for galena shows a maximum with the value decreasing again for the smaller particle size fraction. Repeated determinations resulted in identical results. This may be caused by the very fine particles agglomerating because of residual hydrophcbicity during the flotation procedure, the flocs formed this way being coarser and the entrainment value thus decreasing.

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Figure 11 shows that extremely coarse galena up to about 650 μ m, is readily floated under conditions of relatively high addition of collector reagent, but that the recovery of these very coarse particles drops rapidly as the collector addition decreases. It is seen that the fine particles are readily floated at the relatively high collector additions, and that the recovery of these fine particles decreases with decreasing collector addition (as is to be expected). However, the decrease is not as marked as that occurring under the same conditions for the coarse galena particles of about 850 μ m.

It is of interest to mention that according to Gaudin et al (62, 128), the maximum theoretical size of galena that is floatable is 2100 µm, assuming cubic particles (galena is generally cubic). The coarsest galena particles that have been recovered in practice are about 400 µm in size. According to Figure 11, galena particles up to about $1100 \mu m$ in size were floated albeit under conditions of high collector addition. The reasons for the very coarse particles having floated is due to the unusual flotation conditions existing in the Fuei 'nau cell, viz. low pulp density, the high collector addition vel and the gentle agitation conditions.

Suwanasing and Salman (65) floated galena in a modific Hallimond tube varying the collector reagent additions and the particle sizes. It was observed that as the collector addition increased, the maximum recovery range was extended, particularly towards the coarser particle sizes. In this respect, the results of this investigation are identical to those of Suwanasing and Salman. Under conditions where there was sufficient collector for only one monolayer coverage, these authors obtained a maximum recovery at a particle size of about $55 \mu m$. In this investigation, the maximum recovery was observed at a particle size of about 40 um P ider similar conditions. This small difference can be ascribed to the different techniques employed in the re spective investigations. It should be noted that the results from the present investigation are also well in keeping with the results of other authors as mentioned by frahar and Warren (60).

Comparison of the recovery-particle size relationships of galena and cassiterite immediately shows that the flotation behaviour of these minerals differ greatly. However, this comparison will be more fully discussed in the following section.

4.6 Ultrasonic treatment

During the course of experimentation, it was observed that cassiterite samples that nad been subjected to ultrasonic vibration treatment during the course of their preparation, showed higher flotation recoveries, particularly .n the very coarse sizes, than did the same material which had not been treated by ultrasonics. Because of the implications of this result to the understanding of the floatability of cassiterite particles, it was decided to characterise the ef.ect of ultrasonic treatment more fully.

A coarse Rooiberg cassiterite size fraction (105 to 125 pm) was subjected to ultrasonic treatment over a period of time, some of the sample being withdrawn at fixed intervals. These ... aples were then floated in the normal manner. Figure 19 s ws the results of this test. From this graph it is seen that the longer the sample is subjected to the action of ultrasonics the greater the subsequent total flotation recovery. It can also be seen that although the longest period tested was 15 minutes, it is apparent that the recovery will increase

further still for further extended periods of ultrasonic treatment.

The Rooibery cassiter : sample was then investigated by treating a number of different particle size fractions with ultrasonic vibrations, and then floating these samples. A comparison of the total recoveries of the samples treated with ultrasonics, and the samples not treated with ultrasonics, is shown in Figure 20. The duration of ultrasonic treatment for each size fraction was 15 minutes. From Figure 20 it can be seen that the ultrasonic treatment does not effect the recovery of the finer particle sizes very much since the total recoveries of the untreated samples are already virtually completed. The coarser particle size fractions larger than 50μ m thus show the effect of ultrasonics to the greatest extent and it is apparent that the recovery of coarse particles have been increase: greatly relative to the fine particles.

Cassiterite samples from Union were also treated with ultrasonics, and these samples also show an improved total recovery over the untreated samples in every case. Figure 21 shows the difference between Union samples treated, and those not treated, by ultrasonics. In this case the duration of the ultrasonic treatment was 7 minutes. The results of Union are of the same nature as those for Rooiberg, although the difference between these samples is due to the fact that the ultrasonic treatment time wes less in the case of the Union samples. It should be noted that the identical effect was observed for cassiterite samples from Kamativi and Renison, although no detailed study was made in these cases. Gangue samples of various particle sizes were also treated with ultrasonics, and then floated. Untreated and treated total recovery results ure shown in Figure 22. The duration of ultrasonic treatment in this case was 15 minutes. As can be seen from Figure 22, no great increase in recovery was obtained in this case and the two curves are almost identical. This indicates that the ultrasonic treatment had no significant effect on the gangue .

In order to test the above observations with gangue and cassiterite, a cassiterite and gangue mixture of equal proportions was floated, and the total recovery of cassiterite results compared with the results of the same samples which had been subjected to ultrasonic treatment for 15 minutes. The results are shown in Figure 23, the cassiterite recoveries having been obtained by way of microscope grade estimates of the concentrates. A subsequent chemical analysis of some of these concentrates verified the curves of Figure 23. Consequently it can be seen that the samples treated with ultrasonics presented significantly superior flotation recovery results when compared with the recoveries of normal samples.

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During the ultrasonic treatment of a cassiterite lample, it was observed that a large number of very fine-grained particles were appearing in suspension in the liquid medium together with the cassiterite sample. It appeared as if these particles were being knocked off, or dislodged from,the larger grains. It was assumed that these fine particles were gangue slimes which had been adhering to the large cassiterite grains. A sample of tnis material was collected for chemical analysis. This showed the material to contain 85 per cent tin dioxide. An X-ray diffraction analysis was then performed on this material to determine the mineralogical identity of these very fine particles. It was found that these very fine particles were predominantly cassiterite, while minor amounts of chlorite and mica were also identified. The finding that these fine particles were predominantly cassiterite made it difficult to explain the observed difference in flotation recovery between samples which had been treated with ultrasonics, and those that had not been treated. It could have been that these small particles had been broken off from the matrix off the larger grains during the ultrasonic treatment, or alternately had been very small particles adhering to the surfaces of the larger cassiterite grains. It was thus decided that the scanning electron microscope might be used to investigate some of the observed phenomena.

A sample of the very fine particles which had been separated from the larger cassiterite grains was studied. The sample was shown to contain a very large range of particle sizes ranging from about 0,1 um (which is about the limit of good resolution of the instrument) up to sizes of about 10 pm. Many of the coarse particles present in the sample were observed to be agglomerates of very fine particles. A qualitative analysis of this material showed it to be cassiterite with slightly higher amounts of aluminium, silicon, sulphur, titanium and iron relative to a representative cassiterite grain. The presence of the higher amounts of other elements apart from tin confirms the mineralogical analysis since chlorite and mica are predominantly made up of aluminium, silicon and iron.

A sample of the CTR3 Rooiberg fraction (see table A3, Appendix 2) was also investigated with a view to verifying the particle size of this sample. It was found that some of the particles had agglomerated into coarse aggregates, although individual particle sizes were observed to be of the order of 0.1 µm in size. A qualitative analysis of this sample showed it to he alightly richer in iron, aluminium, silicon and sulphur relative to a grain of cassiterite. This observation is readily understood when it is considered that minerals comprising the above-mentioned elements (for example, pyrite, chlorite, mica, hematite) are softer than cassiterite and are, therefore, m lled to the finer sizes and tend to collect in the finest size fractions.

Coorser particles of cassiterite (105 to 125 µm) were then investigated using the scanning electron microscope in an endeavour to find an explanation for the observed difference in the total flotation recovery for samples treated with ultresonics, and untrasted samples. Two samples were investigated, one having been treated with ultramonics for 15 minutes, while the other sample was an untreated sample. Low magnifications (up to 500) were employed in scanning the two samples with the scanning electron microscope. No physical differences

could be detected on these samples as each showed the same surface features, viz. smooth, flat and conchoidal faces as well as mottled; porous and jagged surfaces. Also no chemical differences could be detected between the samples. It was considered possible that a type of coating could be responsible for the observed differences in flotation behaviour. This coating could have been removed by the ultrasonic treatment. However, no evidence of a coating was observed. This observation could not be considered conclusive since any costings of hydraxide, carbonate or hydrocarbons would not show up in th oalyais. Also, in view of the low magnifications employed, it as decided to prepare new samples and to study these at much higher magnifications.

Samples with particle sizes between 105 and 125 µm were prepared. A sample was treated by ultrasonic vibrations for b0 minutes, while another sample was retained untreated for comparison. Both samples were then scanned by the scanning electron microscope at a magnification of 3000. It was then noticed that the un treated sample showed a very much greater number of very sma 1 particles adhering to the surfaces of the larger grains than did the treated samples. The accompanying photomicrographs show up this effect (see Plates 2 to 13). Higher magnifications than 2000 showed the same effect of adhering fine particles, but a magnification of 3000 gave the best clarity of the photomicrographs. From the photomicrographs it can be seen that these adhering particles cover each grain completely in the case of the untreated particles, and that the coating density of these very fine particles is much greater then in the case of the cassiterite which had been treated with ultrasonic vibrations. As can also he seen from the photomicrographs, the adhering grains have a large spectrum of sizes ranging from less than $0, 1$ μ m (barely observable) to about 5 μ m, and sometimes larger. These are about the same sizes as were observed for the very fine particles which were removed from the coarser grains during the ultrasonic treatment. A large number of these adhering particles were analysed qualitatively with the micro

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probe facility of the scanning electron microscope. The analysis showed that about 80 per cent of the adhering particles are tin-based (cassiterite) while the remainder of the particles are either calcium-rich (perhaps calcite), or silicon-rich (perhaps quartz), or a calcium-silicon mineral (perhaps chlorite or feldspar), or, as was observed in one case, a calcium-silicon-aluminium-magnesium-titanium-iron mineral (a mixture of mica and rutile perhaps). Finally, the fact that approx .ately 80 per cent of the adhering particles are cassiterite confirms the mineralogical analysis of the very fine particles, while the ether elements detected in the analyses of other adhering grains verifies the finding that chlorite and mica are present.

It can thus be stated that the very fine particles which had been removed off the surfaces of larger grains, and those adhering fine particles observed on the surfaces of larger grains are one and the same, since the data is consistent on every count. Thus, it is seen that very fine particles of cassiterite agglomerate with coarser particles, and it is these very fine particles which are removed during the ultrasonic treatment.

Finally, Rooiberg samples which had been treated with ultrasonics were floated to determine their entrainment characteristics. The results are shown in Figure 24. It is seen that the entrainment values in this case are higher than the entrainment values for untreated samples (see also Figure 6). Figure 25 shows the entrainment curve, the total flotation recovery curve and the pure flotation curve for samples treated with ultrasonics. Note that in this case, the pure flotation curve has been transposed to much coarser particle sizes when compared with the true flotation curve for untreated samples. The implications of this finding will he discussed in the next section.

From the graphs featuring the ultrasonic results, it is seen th_t there appears to be some scatter among some of the recovery results. This could have arisen during the course of the experimental technique.

It is thus seen that the ultrasonic treatment of cassiterite is responsible for vastly improved flotation recoveries, both total and pure flotation recoveries, particularly in the coarse particle size range.

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Sample treated with ultrasonic vibrations
(3000 X) PLATE 7

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PLATE 9 Sample treated with ultrasonic vibrations (3000 X)

 $B7$

PLATE 11 Sample treated with ultrasonic vibrations (3000 X)

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PLATE 13 Sample treated with ultrasonic vibrations (3000 X)

5. DISCUSSION

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The aim of this dissertation was to characterise the relationship between particle size and the flotation recovery for cassiterite in regard to both coarse particle sizes (larger than 50 μ m) and very small particle sizes (less than about 7 pm), since it is known that cassiterite between these limits is floatable in practice. An added objective was to determine whether or not cassiterite behaves like other floatable minerals under flotation conditions. Vnat has been achieved will now be assessed.

The flotation cell chosen for this investigation was the fuerstenau cell for reasons which have been d.scussed. It was found that the reproducibility of the cell was very good with the maximum standard deviation obtained being 3,2 per cent, and the highest standard error being 1,5 per cent. It should be appreciated that the conditions existing in this cell cannot be directly compared with either laboratory-scale or industrial-scale flotation conditions because of differences in, for example, pulp density, agitation conditions and aeration rate. However, the Fuerstenau cell does provide an indication *o*'* the tendency of particles to collide and adhere to bubbles which is ideal for an investigation of this nature. Regarding the aspect of entrainment, the problem becomes more tenuous since the mechanical conditions differ markedly between the Fuerstunau cell and large-scale practice. However, trends were shown up using the Fuerstenau cell. It should also be appreciated that the maximum particle sizes which float may differ for different types of cells and under different conditions. However, the Fuerstenau cell did allow the parameter(s) under observation to be characterised. It is apparent that the Fuerstenau cell is suitable for situations where only small amounts of sample are avail ble, as in the case of this investigation. Finally, it may be stated that the results of the present study employing the Fuerstenau cell bear a very good resemblance to those obtained from both laboratory and industrial applications, as discussed in the previous section.

A great deal of work was done in order to characterise the effects of entrainment on the total flotation recovery of cassiterite. To this end it was determined that the cassiterite samples appear to show entrainment in that the values increase with decreasing particle size. It has been assumed that cassiterite possesses no native fInstability and that only entrainment had occurred. Should some degree of native floatability have occurred, or perhaps some reaction of the cassiterite with the frother, it would not be possible to distinguish these effects from entrainment under these conditions. Both gangue and galena samples show a maximum in the relationship between particle size and entrainment recovery. This may be due to agglomerates having formed during the flotation procedure. In the case of the galena samples, pure entrainment only cannot be stated to have occurred and it is considered that some degree of native floatability was retained by the samples even though large amounts of galena depressant had been added to the system.

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As has been mentioned, it is considered that entrainment an a flotation system cannot be suppressed, and hence should be charac teris ed for any investigations of this nature in order to obt in the pure flotation recovery. This has been done for certain samples and tie results *c** the tc I recovery, entreinment and pure flotation are given in Figures 6, 7, 8, 9 and 1C, for Rooiberg, Union, Wheal Jane, Kamativi and guncue respectively. It is to be noted that the pure flotation curves give the shape which many authors regard as standard, that is, as the particle size decreases from some coarse size, the total recovery increases from a very low value to a maximum value, and then decreases again. But it is at the stage of about 2 μ m that experimental data from the literature becomes non-existent and only theoretical considerations remain and can be discussed. However, before these the ries are to be considered, the abovementioned graphs will be discussed to a greater extent.

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As can be seen from the above graphs, viz. Figures 6, 7, 8. 9 and 10, the maximum pure flotation recoveries are at coarser particle sizes than is the case for the total flotation recoveries, the difference being due to the effect of entrainment. Table 4 gives the respective particle sizes. The Wheal Jane sample has much lower maximum recovery particle sizes than the other samples and this occurred because the Wheal Jane sample was of much lower grade. Because of the cyclosizing technique employed for sizing this sample, a density-particle size classification resulted. Thus, although the particle sizes are given relative to the mineral cassiterite, other minerals with lower specific gravities will be much coarser. Thus, quartz particles, for example, may actually be almost twice the size of the cassiterite particles in each of the cyclosizer size fractions. This will result in reduced entrainment effects for each particle size fraction. This effect will thus also influence the pure flotation curve results. It can also be seen from Figures 6, 7, 8 and 9 that at a certain particle size, the entrainment values become larger than the pure flotation values. For Rociberg this occurred at a particle size of about 6 μ m, for Union at about 6 μ m, for Wheal Jane at about 7 μ m, while for Kamativi at about $6 \mu m$. These results indicate the particle sizes at which, for decreasing sizes, the recovery mechanism changes from a predominantly flotation mechanism to that of entrainment. It is, therefore, apparent that flotation of particles smaller than about $6 \text{ }\mu\text{m}$ should be avoided unless the effect of entrainment can somehow be reduced, for example, by washing the froth with a water spray. Also of interest is the fact that if the entrainment curve be extrapolated (assuming this to be feasible) , and hence also the pure flotation curves for both Rooiberg and Union, that the situation is then reached where flotation ceases altogether tor particlu sizes of the order of 0,2 to 0,5 pm. This would imply a recovery purely by entrainment under these physical conditions, and no particle-bubble attachment occuring for particle sizes smaller than say 0,2 pm. However, this is only conjecture as there are no results to substantiate this idea, although it is

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c ^t interest to compare these results with those predicted **by mathematical considerations of the particle bubble attach**ment process. The treatment by Sutherland predicts a zero flotation rate at a particle size of approximately 0,5 μ m, while the theory of Woodburn et al predicts a zero flotation rate at a particle size between 15 and 20 μ m (60).

It is now of value to consider the theories of the effect of particle size on the flotation process as discussed in the literature review. As mentioned previously, the rate of flotation is considered to be equal to the product of three factors, viz. the rate of collision between particles and bubbles, the **Probability of adhesion, and the probability that nc detachment** will subsequently occur. In this investigation, the flotation recovery was measured. Since this is a combination of the three abovementioned factors, the results will be assessed with **respect to each of these ^'actors.**

I. The rate of collision. A brief summary from Trahar and Warren (60) and Jameson et al (61) is given in Table 6, and from this it can be determined which theory fits the results ottained in the beat way if it can be assumed that tne rate of **collision is the dominating mechanism in the flotation process.**

TABLE 6

Theories of the variation of collision rate with **particle size**

Considaring the results of pure flotation recovery for Rooiberg, Union, Wheal Jane and Kamativi as given respectively in Figures 6, 7, 8 and 9, it is apparent that all the above theories, except that of Meloy, fit the data obtained, although it is to be noted that the data holds for sizes down to 3 um only. It is at this point that the **extrapolated curve discussion held above could be discussed** again. On extrapolation, it can be seen that the rate of **the collision of particles and bubbles would tend to zero** for some definite particle size. This conjecture would then fit the theory of Derjaguin and Dukhin best with the reservation that the particle size might not be a critical **size valid to all systems.**

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2. The probability of adhesion. The various factors dictating this aspect will be briefly considered.

According to the theory of Sutherland, the induction period is independent of the particle size. However, **a ccor di ng to Klassen and Mokrousov, longer periods are required for larger particles. These views are still divergent at this stage because of the lack of data.**

The factors which tend to reduce the probab. lity of attachment of fine particles to bubbles are the increased dynamic contact angle and the low momentum of fine particles (less than 10 μ m ir size).

The increased ratw of adsorption of flotation reagents onto fine particles would appear to favour an i^r crease in their recovery in a flotation system. The high surface energy of very fine particles may favour the adsorption of flotation reagents; this in turn would improve the flotation recovery of these very fine particles. However, the extent of adsorption of reagents may vary with particle size. In one of **the few investigations into this aspect, Clement found that** for a particular coverage of collector reagent the recovery **of fine particles was significantly less than for the same coverage of coarser particles. For the system studied, this suggests that very fine particles required more surface coverage for the same flotation recovery.**

The possible different ages of different particle sizes present in a flotation feed pulp is not considered to affect their recovery. Similarly, the thermodynamic solubility of very fine particles is not expected to differ from those of coarser particles, unless these fine particles are less than 0,1 μ m in size (60).

It is apparent tnat the fall in flotation recovery of **particles below the maximum pure flotation recoveries** observed for the various cassiterite samples, as given in Table 4, viz. sizes smaller than 30 μ m, cannot be attributed to changes in surface energies. In fact, it would appear that the effects described in this section caly influence **the flotation recoveries of very fine particles, say smaller** than about 3 µm.

3. The rate of detachment. It has been determined that **under both quiescent or agitated conditions, the flotation** of very fine partirles is not limited w their detachment **from bubbles (60).**

The mathematical combination of the three factors influencing the flotation recovery of a **particular system has led to the conclusion that the flotation recovery decreases** with particle size. In the case of Sutherland, the flotation rate shows no maximum with variation in particle size, increasing as the particle size increases. Woodburn et al obtained **r** maximum flotation rate at a particle size of about 70 μ m, with recoveries decreasing for coarser and finer sizes **(6C). Although there are practical deviations from the results obtained by Woodburn et al, it would appear that their overall mathematical treatment is successful except perhaps for very fine particles where the theory of Sutherland appears to give** more accurate results. It is apparent that the pure flotation **recovery results obtained for the cassiterite samples** investigate ' qualitatively follows the above two theories for **decreasing particle sizes below about 35** *\xm* **in size (see** Figures 6, 7, 8 and 9), and the theory of Woodburn et al for particle sizes coarser than 35 µm in size (60).

Finally, it is apparent that the majority of workers ronsider that recoveries decrease with decreasing particle size. That this is virtually universal can be deduced from the review by Trahar and Warren (60). It can be seen that within the framework of the results obtained in this investigation the **very same conclusion is reached.**

It is also of interest to consider the recovery-particle size results without taking entrainment into account, since, for practical reasons, entrainment is not considered in industrial applications In this case, only the total flotation results of Rooiberg, Union and Renison will be considered since these were taken to smaller particle sizes than the other samples. It can be seen from the results of Union and Renison that, as **the oarticls size decreases, the recovery maximum is followed** by a minimum. Without considering the influence of entrainment, this effect car be explained by the possibility of the particles **agglomerating during the flotation procedure to coarser aggre**gates. These agglomerates would then behave as coarser particles. In the cass of the Rooiberg sample, agglomeration could have **occurred with the small particle size fractions, although no evidence of agglomeration was detected during the flotation** procedure. However, the Rooiberg reuults could also be interpreted as being very similar to those of Gaudin et al (75) obtained when they floated galena. In the case of the present investigation, the results are even more meaningful **since much finer particle sizes were used than Gaudin et el user in their work. Also, in this investigation, the** in rainment results were characterised for the cassiterite system, and deducted from the total flotation results to give the pure flotation results. Gaudin et al (75) did not take into account the entrainment of galena which must have occurred, together with flotation, since these two effects are both inherent to the system at the particle sizes investigated. This is why it is considered that the results of Gaudin et al dc not plesent the true state of affairs of flotation recoveryparticle size in the system they studied. Should these workers **have recounted for entrainment and thus obtained the pure**

f lotation recovery, their results would have fitted any of **tha above-mentioned theories of the variation of collision** rate with particle size, except that of Meloy (as is the case with the results from the present investigation), if it is **ossumed that the probability of the rate of collision be the dominating mechanism of the three factors influencing the** attachment of particles to bubbles. As the results of Gaudin et al are stated in the reference, it appears that the theory of Meloy is the only one that is compatible with them. The above **argument also holds for the results of de Bruyn and Modi (129)** who obtained results of a similar nature to Gaudin et al.

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Pursuing this line of reasoning, that is, to consider the recovery - particle size results without taking the entrainment into account, it is seen that the recent review by Jameson et al (61) contains some interesting new developments. Reay and **Ratcliff, in determining the rate of collision of very small** particles found Brownian diffusion to be the dominant capture mechanism for particle size. smaller than 1 to 2 um. They **deduced that under Brownian diffusion, the rate of collision decreases with increasing size until, when only the hydrodynamic** furces come into being, the rate increases again. Thus a minimum is obtained in the collision rate at a particle size of about 5,6 μ m. However, in determining the above theory, Reay and Ratcliff oversimplified the assumptions. Collins (61) **corrected for these oversimplificatione and the result was that, altnough the minimum in the predicted collision rate still oc curred at about 0,6 pm, the magnitude of the collision rate was** higher. With this information it is interesting to note that the results of Rooiberg, Union (Ficure 12) and Renison (Figure 14) **could fit the theory of Collins.**

A further consideration is that the total flotation **recovery minimum corresponds to the point beyond which, for nmaller particle sizes, entrainment becomes the major mechanism** of total recovery, and pure flotation by bubble - particle attachment is reduced to very low or negligible values. Further decreases in particle size would then lead to increasing entrainment values.

It should also be noted that it appears that smaller

bubble sizes will result in improved bubble-particle collisions and subsequent attachment (61). This variable, **bubble size, cannot usually be altered in the current flotation techniques, and this factor was also uncontrollable during the course of this investigation. It could have been** that the recovery of very coarse galena may have resulted from **very coarse bubbles being present in the flotation cell,** Loncomitantly this would have reduced the recoveries of very **fine particle sizes.**

It can be brisfly mentioned that the samples of cassiterite **which responded best to (total) flotation were those which** contained the least amounts of iron, viz. Kamativi, Zaaiplaats and Uis. Since these cassiterite samples were virtually pure, it appears that the iron analyses of these samples relationships regarded as substitution iron and not bulk iron present in .n. sample. This observation, although not a definite rule, **appears to be at variance with those authors who claim the** presence of iron to be beneficial to cassiterite flotation **(see 29) .**

Regarding the effect of collector concentration, Figure 2 shows that increasing the collector concentration has little **01 no effect on the recovery of small particle sizes above about 500 mg/1 EPPA initial concentration. However, for** coarse sizes larger than about 100pm, it uppears that increases in the collector concentration result in further increases in **the recovery. This result is in accord with the findings of Mitrofanov et al (130, 131), viz. that coarse oarticles require** a greater density of collector reagent coating than fine **particles of the same mineral in order to attain reasonable recoveries. This effect was also very apparent for galena** since an increase in the collector concentration increased tho flotation response of the coarser particles predominantly (see Fiqure 11).

It is of great interest to compare the recoveries of the **cassiterite samples which had been subjected to ultrasonic** treatment, and those samples which had not been treated. It is apparent that the effect is beneficial to flotation recovery

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ell cases fince thu recoveries for the ultrasonic samples are in each case higher than the normal sample recoveries. This beneficial effect is particularly evident for the **coarser cassiterite samples (larger than 50pm) which are** ronsistently a fected this way. Also, according to Figure 22, the ultrasonic effect seems to have very little influence **cn gangue.**

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As *far* **as can be ascertained, the ultrasonic effect described above has not been observed previously for cassiterite. Agranat et al (116) have reported vastly** increased recoveries for the minerals chalcopyrite, jarosite **and 1 imonite, while the recoveries for molybdenite and quartz** We a reduced with increasing sonification periods. This has **been discussed in the literature review.**

From the scanning electron microscope photomicrographs, it appears as though the most direct explanation is that the **very fine particles adhering to the large cassiterite grains somehow interfere with the flotation of these larger grains** which are normally floatable, that is, in the absence of these very fine particles. Figure 2 shows that for coarser particles. the total recovery can also be increased by increasing the amount of collector reagent. However, it appears that the **adhering ultrafine particles somehow prevent the flotation** of coarser par licles. It could be that the particle **bubble adhesion is prevented by the presence of these ultrafines. However, other explanations may be found for this phenomenon and it could be that these ultrafine, predominantly** cassiterite, particles . a merely incidental. Thus some ch. mical coating, for example, an oxida or organic coating **may be removed during the ultrasonic treatment in addition to these ultrafine particles, and this might be the reason for the improved recoveries that were obtained. Not much can** be said about organic coatings should they exist, although **it would** be **expected that the ultrasonic treatment would have removed such coatings. Organic coatings thus appear to** be **highly unlikely as being the cause of the initially poor flotation response shown by the cassiterite. Also,** cassiterite is chemically very stable and it is therefore difficult to

consider any chemical film formation on the mineral, However, it is possible that the surface of the cassiterite m ay hydrolyse to SnO₂.xH₂O, or, in the presence of iron, to (Sn, Fe) (0, OH)₂, both of which are compuunds known to exist. On the other hand, the explanation may lie in the fact that **the surface free energy of the cassiterite surfaces have een increased markedly by the ultrasonic treatment resulting** in a greater reactivity with the collector.

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However, irrespective of the explanation, there is no doubt that the effect is a very definite one and that this could have practical benefits. These benefits could arise in that the coarser particles could be induced to give greatly **improved recoveries over those obtained at present since the** ultrasonic treatmen⁺ does not have a great effect on the gangue. **This would certainly result in economic savings since the coarse particles are currently lost in the flotation circuit (consider** the results of the Union concentrator in Appendix 5, Table A23, Figure 18, where it has been determined that the recoveries for the coarse sizes, above about 32 μ m, are less than 35 per cent). The above statement is further exemplified by the **following results obtained from the Rooiberg cassiterite s ample.** The total flotation recovery of cassiterite was found to have a maximum at the particle size range of about 9 to 14 pm. When the entrainment values are considered, it is found that **the maximum pure flotation recovery occurs at about 30 to 32 pm. Should the samples be treated with ultrasonic** vibrations, and consideration be given to entrainment, it is **found that the maximum pure flotation recovery has now been** stifted to about 130 to 140 µm (see Figures 6 and 25). **Further evidence of the practice! potential of ultrasonics** are the results obtained for a cassiterite and gangue mixture. **Although the whole samnle had been treated with ultrasonics, the cassiterite recoveries showed much improved results over samples which had not been treated with ultrasonics.**

The ultrasonic results imply that the coarse cassiterite particles (larger than 50 pm in size) are indeed floatable, **contrary to the results obtained by other cuthors as mentioned**

in the literature review. It is apparent that the flotation conditions, as they exist in practice at present, are not conducive to the flotation of coarse cassiterite.

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It has, therefore, been observed that there are two .Bible **waya of** increasing the recoveries **of** coarse particles, viz. by increasing the collector reagent addition, **by ultrasonic treatment. From the apparent mechanism** of the latter method, that is, the removal of ultrafine **Bring particles and the subsequent improved flotation** response, comes a further pessible method of increasing the recoveries of coarse particles, viz. by the use of a very efficient diapersing agent. This dispersing agent might well be able to disperse all the particles to such an extent that the slime will not adhere to the surfaces of the larger grains. The efficiency of any dispersing agent can easily be gauged by the amount of coarse particles appearing in the concentrate, that is, the more efficient the dispersing agent, the greater the recovery of the coarse particles.

rinally, it is of interest to mention that Akopova et al (117) also observed that very fine particles were removed from the surfaces of larger greins, although the larger grain **surfaces themselves were not investigated as was done in this** study. The sizes of these removed particles were found to be hexween 0,3 and 0.5 µm. The sizes of the particles removed from the large cessiterite grains in this investigation varied from less than 0,1 to 10 µm although the great majority of particles were less than 0,5 pm in size. It is, therefore, **ap parent that Akopova et al observed the identical effect of** ultrafine particle removal off the larger grain surfaces. Also, an analysis of this ultrafine material by Akopova et al was found to dif er slightly from that of the bulk sample. This is identical to the effect obtained during this investigation where the ultrafines had an analysis of 85 per cent tin **dioxide, whereas the bulk sample showed 95,3 per cent tin** di oxide.

In conclusion, it should be stated that the effect of **ultrasonic treatment on mineral** samples has **not yet been**

illustrated before by means of photomicrographs as was done in this text. Although a number of workers have **observed slime coatings on particles, the correlation of** ll otation response for particles with a large number of adhering slime particles, and with a greatly reduced number of slime **particles on the surfaces of larger grains, had not been done** before as was performed in the case of this investigation, that is, by the observation of the surfaces of particles.

It is apparent that the flotation behaviour of t assiterite, and that of a mineral like galena, differs greatly. Whereas galena is readily floated by xanthate **collectors, no specific collector for cassiterite has yet** been manufactured despite a variety of claims made to this effect. The collectors currently in use for collecting **cassiterite are not entirely specific for cassiterite alone and may float hematite, rutile, fluorite and tourmaline into the concentrate as well. Also,whereas very high concentrate** grades of many minerals are generally readily obtained in practice, it is not common practice to exceed 45 per cent. cassiterite grade in the flotation concentrate. Further, considering the collecting ability of EPPA, it has been shown in this investigation that the reagent is, under normal flotation conditions in practice and laboratory conditions, **not capable of floating coarse particles larger thgn about** 50 µm even at excessive collector additions. It is only **after ultrasonic treatment that the rPPA can float these** coarse particles. This poor flotation capability of EPPA is **in keeping with the results of various workers who found the** above effect during the course of their work (3, 14, 18, 20 41, 93). In the case of galena, it was found that 100 per cent recoveries could be readily attained, especially in the **presence of sufficient collector for several monolayers coverage at least, where even very coarse particles of up to** 600 µm it. size gave maximum recoveries. In the case of cassiterite, 100 per cent recoveries were never obtained in **spite of using very high collector additions and using ultra**sonic treatment to improve the recovery values. Also, it

should be noted that the collector additions to cassiterite were in excess of those applied to galena.

The maximum total flotation recoveries of the two minerals were found to occur at di fferent particle sizer. In the case of galena, this maximum was found to occur at about 40 µm, while for cassiterite it was much lower, viz. about 15 μ m. The entrainment characteristics for the two minerals are also different, as has been discussed. The **entrainment values for galena do nut appear to follow the logical pattern of increasing with decreasing particle size,** as does cassiterite. It is possible that some degree of **agglomeration of these very fine particles of galena had occurred which would then result in an apparently anomalous value being obtained, although some degree of native floatability may, in fact, be responsible. The effect of agglomeration can, in fact, not be ruled out for any of the very fine particle sizes as this could nave taken place during the course of the flotation test, even though no evidence of** this was observed. For the cassiterite samples, the ultrasonic action would have broken up any agglomerates if these had formed, and hence be responsible for the higher entrainment values obtaine^t when compared with the entrainment values for **normal samples (see Figure 24). However, this could have occurred for the very fine particle sizes, but not for the coarser particles, and Figure 24 shows higher entrainment values for the ultrasonir samples for both the coarse and the** fine particle sizes. It is thus apparent that effects other than the one just described are responsible for the different **results obtained.**

Notwithstanding the above-mentioned differences between galena and cassiterite, it is apparent that the galena and **cassiterite flotation tudies were performed under the idential physical conditions prevailing using the equipment** already discussed. It is thus seen that a comparison between the two minerals is, in fact, valid. From this comparison it **is immediately evident that the two minerals, galena and** cassiterite, behave totally unlike each other. A cause of

this difference would well lie in the fact that casaitarite can be host to a number of elements which isomorphously substitute for tin within the crystal lattice. This has been discussed at length in the literature review. The spectrographic analysis performed (Table 5) shows that each cassiterite sample contains a number of impurity elements. That these elements may alter the floatabilities of these cassiterites has, however, not been proven. In contrast, galena appears to exist as a much more horogeneous mineral than cassiterite, and substitution for lead by other elements appears to be negligible, although the geological environment will apparently cause differences in the behaviour of galena with respect to xanthate adsorption and oxidation (132). Finally, it is interesting to note that the cassiterite samples treated with ultrasonics have greatly improved flotation recoveries, and the behaviour of these samples begins to approach that of the galena samples.

Warren (106) found that ultrafine particles of scheelite (less than 1 µm) adhered to larger (between 10 and 40 µm) grains of acheelite, but that the flotation recovery of these coarser acheelite grains was not adversely effected by the presence of these ultrafines. These ultrafines were found to adhere to the coarser grains as a result of non-electrostatic forces since all the particles had the same charge. If it could be considered that the ultrafine cabsiterite particles adhering to the coarser grain surfaces result in an identical fashion as was the case for the scheelite, it is seen that in the case of the cassiterite, the difference in flotation behaviour in significant in the size range of 10 to 40 um, but more empecially an for the coarser grain sizes (see Figure 20 for the Rooiberg results). It would thus appear that although the mechanism of fine particle attachment is identical, cassiterite yet seems to behave in some different fashion, as was the case in the comparison with galena. It while the interesting to have observed the flotation behaviour of the theelite after the ultrafine particles had been re aved by ultrasonic treatment. Should the flotation

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recoveries not have been improved by the action of ultrasonics, the explanation could be that the collector used for the scheelite, sodium oleate, is a stronger one ... scheelite than EPPA is for cassiterite.

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It is also interesting to compare the recovery - particle size curves obtained for the various cassiterite samples. It is seen that, although generally the behaviour of the different cassiterite samples is identical, there are small differences. However, this has been elaborated on in a previous section where it was postulated that the geological character of the **cassiterite may be responsible since neither the iron content,** the degree of crystallinity, nor chemical differences could **adequately explain the results obtained.**

It is thus seen that the major aim of the thesis, that is, to characterise the relationship between particle size and flotation recovery for cassiterite, has been achieved in some detail. It has been observed that for small particles, the effect of entrainment becomes increasingly greater with **decreasing particle size until it appears that pure flotation** virtually ceases and all recovery is by entrainment. There therefore appears to exist a lower limit of partiale size **beyond which flotation is not recommended unless the effect** of entrainment can be countered or reduced. Thus, for the very fine particles of cassiterite, say smaller than 2 μ m, it is felt that alternative treatment methods may be more **beneficial, for example, selective ^Inoculation or agglomerate** flotation. For the coarser particle sizes of cassiterite, it **has been shown that particles between 50 and 200 pm can be floated contrary to all previous experimentation employing PPA as the collector reagent. The mechanism which apparently** serves to act to counter the above finding is discussed at **length.** A **secondary aim of the thesis was to determine whether cassiterite behaves like any normally floatable mineral under** flotation conditions. Galena was chosen as the mineral with which a comparison was to be made since galena represents the minerals that are readily amenable to cuncentration by flotation. In this regard, it was determined that the flotation behaviour of cassiterite is totally different to that of galena.

6 . CONCLUSIONS

1. The Fuerstanau microfletation cell has been **found to give very reproducible results. There exists good accord with the results obtained in this investigation and those from practice.**

2. The effect of entrainment is found to bucome non-negligible for particle sizes below about 45

3. The effect of entrainment is to give higher **recovery values than should have occurred had pure flotation only taken place.**

4. Entrainment is found to become the dominating recovery mechanism for particles smaller than about 6 pm.

5. The particle size for the maximum pure flotation recovery is higher than that for the total flotation recovery, that is, about 20 to 30 μ m for the former and about 10 to 20 $µm$ for the latter. This is due to the effect of entrainment. The recovery - particle size data for concentrators is generally given as the total flotation recovery.

6. Coarse particles of cassiterite, larger than **5U** *yum,* **give poor total flotation recoveries under normal flotation conditions.**

T. The recovery - particle size relationship for pure **flotation recovery follows the normally accepted curve,** that it, as the particle size decreases, the recovery increases to a maximum value, and then decreases again.

8. Many workers give only the total flotation recoveries **and ivnore the effect of entrainment.**

J. Different natural cassiterite sumples respond **differently under identical flotation conditions.**

10. Ultrasonic treatment increases the floatability of cassiterite, particularly the sizes larger than 50 μ m.

11. The mechanism for improved floatability apparently stems from the removal of ultrafine particles (predominantly less than 0,5 µm in size) from the surfaces of coarser particles. These **ultrafines are considered to adhere to normally floatable**

particles and prevent these from floating.

12. The majority (about 80 per cent) of these ultra**fine particles are cassiterite.**

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13. The use of the scanning electron microscope to **observe the surfaces of particles which have, and which have not,been treated with ultrasonics, and the correlation** to the subsequent flotation recovery, appears to be unique. 14. The favourable effect of ultrasonic trr.tment **on cassiterite has not been observed before.**

15. The pure flotation recovery - particle size **relationship for ultrasonically treated samples shows a** maximum recovery at about 130 to 140 μ m.

16. Cassiterite floats very poorly when compared **with the flotation behaviour of galena. Ultrasonically** treated cassiterite has a much improved flotation response. **particles and prevent these from floating.**

12. The majority (about 80 per cent) of these ultra**fine particles are cassiterite.**

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13. The use of the scanning electron microscope to observe the surfaces of particles which have, and which have not, been treated with ultrasonics, and the correlation to the subsequent flotation recovery, appears to be unique. 14. The favourable effect of ultrasonic treatment on cassiterite has not been observed before.

15. The pure flotation recovery - particle size **relationship for uItrasonically treated senoles shows a** maximum recovery at about 130 to 140 pm.

16. Cassiterite floats very poorly when compared with the flotation behaviour of galena. Ultrasonically treated cassiterite has a much improved flotation response.

RECOMMENDATIONS FOR FURTHER WORK

The ultrasonic treatment of cassiterite samples has been shown to impart a greater degree of floatability to the **cassiterite, the effect being most prominent in the coarser particle size range where, under normal flotation conditions** cassiterite has only a poor tu negligible flotation recovery. That the ultrasonic treatment could be employed to reduce the losses of coarse cassiterite particles in the flotation **circuit seems apparent. Also of interest is the fact that** gangu^e cypcui3 to be largely unaffected by ultrasonic treatment. It is consequently falt that ultrasonic treatment situald, therefore, be carried out on concentrator matet Le¹ and also be extended to actual plant conditions where the greatest amount of information on the system will be obtained. It is advocated that an ultrasonic transducer **be tested prior to the desliming circuit so that any ultrafine oarticles which are knocked o*f the larger particles may be removed from the flotation circuit in the discarded slimes.** A **further point of application for an ultrasonic** transducer is prior to the addition of the dispersing agents **(so that the ultrafinea knocked off may remain dispersed), and the addition of modifier and collector reagents so as** to obtain the maximum benefits of these reagents on the **cassiterite particles.**

Finally, in an investigation of this nature, it would **be advantageous to obtain the flotation recovery values at** various flotation times, as has been done by Trahar (60) **and Anthony et al (64). This method of presenting recovery** results has a number of advantages over the system employed **in the present investigation, not least being that more** information about the kinetics of the system may be obtained **in this manner.**

APPENDIX 1

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 $v = \frac{2 (d - d_0) \pi^2}{93}$ **v** = $\frac{2 (d-d_0) \text{ gr}^2}{9 \text{ ?}}$
where **v** = settling velocity (cm/sec) The calculation of particle sut-point sizes during centrifuging **Stoke's Law is given as,** r *x* radius of particle (cm) d = density of mineral (g/cm³) do = density of medium (g/cm³) $g = gravitation$ acceleration $(c m/sec²)$ \hat{J} = viscosity of medium in poisrs (gm/ cm sec) **tor centrifuges, Also** $v^4 = \frac{1}{100} = v \times 60$ where v^1 = settling velocity (cm/min) L = settling distance (cm) t = centrifuging period (mins) K * cantrifuging constant which depends on **the configuration of the centrifuging** arm. K is giver empirically by, $K = R²(8, 6)$ (0,0000284) where $R =$ revolutions per minute (rpm) Data: $d = density of resistance = 7,0 g/cm³$ **u**o = density of distilled water = 1,0 g/cm we have t **g = 9 8 0 c m / s e c ' | = 0 , 0 0 8 9 4 p o i s e at** 25°C At 900 rpm and a centrifuging period of 12 mins. $K = (900)^2 (8, 6) (0, 0000284)$ **- 1 9 7 , 8 3** Thus for a settling distance of 13 cm. **1 (13) (12) (197 , 8 3)**

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0,005476 cm/min.

Thus $v^2 = \frac{(27(6)(980)r^2}{600}$ (9)(0,00894) = ^ * 0054 76 1 / **2** $= 6,244 \times 10^{-10} \text{ cm}^2$ $r = 2.5 \times 10^{-5}$ cm . Diameter of particle is $5,0 \times 10^{-5}$ cm $= 0,5$ micron.

ill

0,5 micron was the first cut-point obtained on centrifuging.

At 1 , 0 0 rpm and * centrifuging period of 3 5 mins we have: \blacksquare

K = $(1300)^{2}(8,6)(0,0000284)$ $= 412,766$ Thus for a settling distance of 13 cm. *S12L* (35)(412,766) $= 0,00090 cm/min$

Thus ,

$$
v^1 = \frac{(2)(6)(980) \pi^2 (60)}{(9)(0,00894)} = 0,00090
$$

 \therefore $r^2 = 1,026 \times 10^{-10} \text{ cm}^2$

- \therefore r = 1,014 x 10⁻⁵ cm
- \therefore Diameter of particle is 2,028 x 10⁻⁵ cm $\blacksquare = \square$,2 micron

0,2 micron was the second cut-point obtained on centrifuging.

APPENDIX 2

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Particle size fractions employed for the various samples

TABLE A1

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Tyler mesh size fractions used in the investigation

TABLE A2

CONTRACTOR

Rooiberg gravity concentrate sub-sieve sample sizes

TABLE A3

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CY2 20,5 - 14,0 17,3
CY3 14,0 - 10,3 CY3 14,0 - 10,3 12,2
CY4 10.3 - 7.3 8.8 CY4 10,3 - 7,3 8,8

CY5 7,3 - 5,7 6,5
CTR1 5,7 - 0.5 3.1 CTR1 5,7 - 0,5 3,1
CTR2 0.5 - 0.2

Rooiberg sub-sieve sample

Union sub-sieve sample sizes

Zaaiplaats sub-sieve sample sizes

Kamativi sub-sieve sample sizes

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Sample designation	Particle size range (micron)	Median (micron)
CY1	$25,0 - 22,8$	23,9
CY2	$22,8 - 17,3$	20,1
CY3	$17,3 - 12,2$	14,8
CY4	$12, 2 - 8, 8$	10, 5
CY5	$8,9 - 6,5$	7,7
CY6	Minus 6,5	3,25

TABLE A7

Uis sub-sieve sample sizes

TABLE A8

Wheal Jene sub-sieve sample sizes

TABLE A9

Gangue sub-sieve sample sizes

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Galena particle size fractions

APPENDIX 3

Calculation to determine the monomolecular coverage of a collector reagent on a mineral

A3.1 Xanthate on galena

Consider the cross-sectional area of a xanthate molecule to be 30 $\frac{2}{30}$ = 30 x 10⁻⁸ μ ².

Assume the galena particles to have cubic form.

Assume a particle size of 12 pm.

Area of cube = $6 \times 12 \times 12 = 864 \text{ m}^2$

For 70 ml solution containing 100 mg/l initial concentration of xanthate, have

> 70 1000 **C** 7 mg xanthate

The molecular weight of sodium ethyl xanthate is 144,19 (molecular formula C₂H₅OCS₂Na)

Thus have $\frac{1}{144,19}$ millimoles xan hate

The total surface area of xanthate available is,

$$
\frac{1}{144.19} \times 6.02 \times 10^{20} \times 30 \times 10^{-8}
$$

8.77 × 10¹² molecule μ m²

Assume homogeneous packing for galena. Then the mass of one galena particle = $7,5 \times 12^3 \times 10^{-12}$ $= 1,296 \times 10^{-8}$ g

Thus the total area of one gram of galena, 064_______ $1,296 \times 10^{-7}$ 666,67 \times 10° μ m /g

g - nominal coverage in monomolecular layers of xanthate per gram of galena = $\frac{8.77 \times 10^{12}}{9}$ $666, 67 \times 10^{8}$ $= 1,315 \times 10^2$ ≈ 131

A3.2 EPPA on cassiterite

Consider the cross-sectional area of a phosphonic acid molecule to be 30 $\frac{2}{30}$ = 30 x 10⁻⁸ μ m².

Assume the cassiterite particles to have cubic form.

(1) Assume a particle size of 12 μ m.

Area of cube = $6 \times 12 \times 12 = 864 \text{ }\mu\text{m}^2$ For 70 ml solution containing 500 mg/l initial concentration of EPPA, have $\frac{70}{1000}$ x 500 = 35 mg EPPA

The molecular weight of EPPA is 162,13 (molecular formula $C_2H_5C_6H_4P0$ (GH) $_2$).

> Thus have <u>the millimoles</u> phosphoni acid. 162,13

The total surface area of EPPA available is,

 $\frac{35}{162,13} \times 6,02 \times 10^{20} \times 30 \times 10^{-8} = 38,99 \times 10^{12}$ molecule μ m² Assume homogeneous packing for cassiterite. Then the mass of one cassiterite particle = $7.0 \times 12^{3} \times 10^{-12}$ = 1,21 x 10⁻⁸ g

Thus the total area of one gram of cassiterite $\frac{864}{1,21 \times 10^{-8}}$ 714,05 x 10⁸ μ m²/g

8 nominal coverage in monomolecular layers of EPPA 714.05×10^8 546 per gram of cassiterite

 (2) Assume a particle size of $2 \mu m$.

Then employing the same technique as above, have $\theta = 90$.

(3) Assume a particle size of $0.2 \mu m$.

Then employing the same technique as above, have $\theta = 9$.

APPENDIX 4

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The statistical data were calculated using the following formulae,

Mean x =
$$
\frac{1}{n}
$$
 $\sum_{i=1}^{n} x_i$
\nVariance S² = $\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2$
\nStandard deviation S = $\left[\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2\right]^{1/2}$
\nCoefficient of variation, $\bar{x} = \frac{1}{2} \times 100$

Standard error of mean $rac{5}{\sqrt{1}}$

APPENDIX 5

Results of the investigation

TABLE A13

Results of Figure 2

T A B L E A 14 Results of Figure 3

TABLE A15

Results of Figure 4

TABLE A16

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Total and pure flotation recoveries and entrainment values for cassiterite samples from Rooiberg (see Figures 6, 12, 15, 20, 24, 25)

Flotation conditions : Standard

Flotation conditions : Standard

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TABLE A17

TABLE A18

Total and pure flotation, and entrainment values for cassiterite samples from Wheal Jane and Kamativi. (See Figures 8, 9, 13, 16)

Flotation conditions : Standard

TABLE A19

Total flotation recoveries for cassiterite samples from Renison and Rooiberg gravity concentrate. (See Figures 13, 14, 16, 17)

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Flotation conditions : Standard

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TABLE A20

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Total cassiterite recovery for flotation from a gangue/cassiterite mixture. (See Figure 23)

Cassiterite sample : Flotation conditions: Rooiberg Standard

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TABLE A21

Total and pure flotation, and entrainment values for gangue (See Figures 10, 22)

Flotation conditions : Standard

TABLE A22

Total flotation recoveries for galena (See Figure 11)

Flotation conditions : Standard

* 1000 mg/l potassium dichromate

TABLE A23

Typical flotation data at the Union Tin Mine concentrator (See Figure 18)

Flotation conditions

Flotation feed Final tailings Concentrate grade

Conditioning time EPPA consumption Other reagents used

pH Pulp density

: \sim 0,95% Sn (\sim 98 $\scriptstyle\rm \sim$ minus 43 μ m) $:$ \sim 0,40% in : ~ 26% Sn (1 rougher and 3 cleaner flotation stages) $: \sim 10$ minutes : 0,2 to 0,3 kq/t : Sulphuric acid Sodium flouride Sodium silicate \mathbf{r} : ~ 10% solids (cleaner flotation circui t) $-25%$ solids (rougher flotation circuit)

TABLE A24

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Effect of ultrasonic treatment time on flotation recovery (See Figure 19)

Particle size Sample Flotation conditions **105 - 12 5 jim** Rooiberg Standard

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m

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