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DEPARTMENT OF MINES,
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RESEARCH AND DEVELOPMENT BRANCH.

CONTACT PROCESS.

PROGRESS REPORT NO. 1.

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1. SUMMARY.

Features of the process have been demonstrated to senior members of various Sections.

Preliminary laboratory tests for the recovery of cassiterite were carried out on part of a 4-ton parcel of Maranboy ore containing 2.1% Sn. A further 10-ton parcel has been received for test purposes.

The cassiterite in this ore conforms favourably with the basic principle of the process, in that its inherent surface energy is such as to cause marked preferential adhesion over the major gangue constituents to a neutral selector.

The degree of preferential adhesion, under physico-chemically neutral conditions and set selector volume and time, is indicated by the collection, in a concentrate of about 30% Sn, of 50% of the cassiterite representing the finer particles in a size fraction minus 76 microns (200 mesh) plus 20 microns assaying 3.65% Sn and containing an unknown proportion of composite grains.

The force of adhesion can be increased by activating the surface of the selector with oleic acid to give visually complete collection of the cassiterite from a pulp of the same ore treated in the same manner and not conditioned for selectivity. Tailing assays show an actual recovery of 80% in a concentrate carrying 7.5% Sn, the apparent difference in recovery is due to the test conditions and limitations of the apparatus for quantitative work.

Organic matter in the tap water adversely affects mineral-selector adhesion to a degree that the water requires correction.

The reagent-technique apparatus in which the preliminary test work was done is unsuitable for quantitative work. Laboratory apparatus has, therefore, been designed for testing batch charges of pulp with continuously flowing circuits. The apparatus is 50% assembled.

2. INTRODUCTION.

This report describes investigations conducted in the six-month period ended 30/6/59.

The month of January was spent mainly in furnishing the new laboratory with basic equipment.

During the month a parcel of Maranboy tin ore, weighing approximately 4 tons, was received from United Uranium N.L. for test purposes. Two-thirds of the parcel had been contaminated with diesolene from the containers, and this portion was segregated and stored. The remaining one-third had been packed in drums originally containing petrol. The contents were examined, and, after part had been rejected, the ore was crushed from minus $1\frac{1}{2}$ in. as received to minus $\frac{1}{4}$ in. . Twenty-five percent. of the crushed material was cut out for a working sample. This sample, weighing 590 lb., was further reduced to minus 10 mesh. The assay value was 2.10% Sn.

A mineralogical examination was made of the lumps of ore as received, and of the minus 10 mesh material (Report No. P.R.C. 7/59). The composition of the minus 10 mesh material is given as follows:

Quartz	82.5
Tourmaline	14.0
Cassiterite	0.5
Felspar	Traces
Haematite and Limonite	2.0
Micas	1.0.

In view of the contamination mentioned, another sample of ore was requested from United Uranium N.L., and a parcel of 10 tons was received in March.

Experimental work was started at the beginning of February on a control scheelite ore from Kalgoorlie for the purposes of:

(1) Initiating Mr. L. Bollen into the principles of the process.

(2) Devising means for demonstrating to senior representatives of various Sections features of the process characterised in the continuous and discontinuous phase methods.

(3) Determining the effect of Adelaide tap water on the natural selective adhesion of minerals to the selector.

Concurrently, part of the Maranboy working sample was prepared for testing.

3. TEST MATERIAL.

3.1 Scheelite.

The control scheelite ore is a gravity tailing, sizing minus 200 mesh and assaying 4.6% WO_3. The major gangue constituents are iron oxides, iron carbonate and quartz. The material was used both deslimed and containing its full size range.

3.2 Cassiterite.

500 gm. batches of the Maranboy working sample were stage ground in a clean laboratory ball mill, with tap water, to an arbitary grind of minus 48 mesh. A screen analysis of the ground material and tin distribution is shown in Table 1.

Table 1.

Screen Analysis and Tin Distribution.

Mesh Tyler.	Wgt. %	Sn. %	Distribution %
+ 65	4.4	2.95	6.2
+ 100	12.9	1.96	12.0
+ 150	13.4	2.30	14.6
+ 200	8.7	2.30	9.5
- 200	60.6	2.00	57.7
Composite:	100.0	2.10	100.0

The minus 200 mesh (-76 µ) material was divided into two fractions, plus and minus 20 microns, calculated for cassiterite, by beaker decantation. A size analysis is shown in Table 2.

Table 2.

Size Analysis of minus 200 mesh Material.

Microns	Wgt. %	Sn. %	Distribution Sn. %
- 76 + 20	36.2	3.65	61.4
- 20	63.8	1.30	38.6
Composite:	100.0	2.15	100.0

The separations were made in tap water, demineralised water and distilled water.

The minus 76 plus 20 micron fraction was used for initial testing.

4. REAGENTS AND WATER USED.

4.1 Selector Medium.

Liquid paraffin (Ondina 33)
Specific Gravity - 0.884 at 60° F.
Viscosity - 729 secs. RI at 70° F.

4.2 Selector surface activator (molecular link).

Oleic acid.

4.3 pH regulator and gangue repellant.

Soda ash.
Sodium silicate.

4.4 Water.

Tap.
Demineralised.
Distilled.

5. EXPERIMENTAL PROCEDURE.

5.1 Scheelite.

For the purposes (1) and (2) mentioned in the Introduction, ten tests (Nos. 1 to 10) were made on the control scheelite ore in stoppered measuring cylinders (discontinuous selector phase), to show, firstly, the natural and preferential adhesion of scheelite to liquid paraffin under neutral conditions, that is, with surface-inactive paraffin in distilled water; and to show the effects of a suitable reagent balance to increase the force of adhesion of scheelite to improve recovery, and to increase selectivity by repulsion of the gangue minerals, especially iron oxides and carbonate which adhere in preference to quartz.

A clean concentrate with visually complete collection of scheelite was attained, at 20% solids and pH value of the pulp 10.1, with the following reagent concentrations (Test No. 9):-

Oleic acid	0.04 gm./l.
Soda ash	1.25 "
Sodium silicate	0.375 "

For the purpose (3) mentioned in the Introduction, the above tests were repeated using tap water instead of distilled water (Tests No. 11 to 26).

Under neutral conditions other than the tap water, the force of adhesion of scheelite is reduced.

Under the conditions of the tests it became evident that the water possesses a repellant property which, in the presence of oleic acid, has less effect on quartz than on scheelite and the ferruginous material, and the effect is overriding in the reagent system and concentrations used.

With the same reagent concentrations as shown above (Test No. 9), there is no solids adhesion in the selector interface.

With increased concentration of oleic acid, scheelite is collected, but with increased collection of quartz instead of the ferruginous gangue.

The above effects were not countered by varying the concentrations or relative concentrations of oleic acid and sodium silicate.

Soda ash has no repelling effect in the absence of sodium silicate.

In this series of tests with tap water the concentrate, comprising quartz and scheelite, is remarkable for its whiteness, due to complete repulsion of ferruginous gangue.

The effect of the tap water was not changed by pre-treatment with soda ash. A considerable amount of precipitate was formed and the water clarified.

For comparison of demineralised with tap water and distilled water, Test No. 9, using distilled water, was repeated with demineralised water. The results were identical. Demineralised water was used in further tests because of availability.

5.2 Cassiterite.

Preliminary test work on the Maranboy ore was started at the beginning of February.

The size fraction minus 76 plus 20 microns was used for ease of observation and because it is considered more difficult to treat than the finer fraction. The tests were made in the same manner, using stoppered measuring cylinders, as for the scheelite tests and with the same reagent combination. The preliminary test series, using demineralised water for the pulp, is numbered 31 to 60.

For the initial test, the ore fraction was sized in tap water, filter washed with distilled water and oven dried.

Under neutral conditions other than the demineralised water, there is pronounced selective adhesion of cassiterite in this ore to liquid paraffin. The concentrate was estimated at 30% Sn and the recovery at 50% (Test No. 31).

Under the same test conditions, but with the ore sized in tap water and oven dried, both grade and recovery were estimated at half the above figures. Drying in tap water had a detrimental effect on extraction. The test ore, therefore, was sized in demineralized water for this series.

A repetition of Test No. 31 carried further by successive passes, made by removing the laden selector and replacing with the same volume of neutral selector, indicates that a high recovery of cassiterite might be attained from this ore under neutral conditions, as a rougher concentrate, if treated stagewise with control of selector interfacial area. Even with similar area provided in each of four passes in the test, the ore was upgraded. The results, estimated visually and calculated on weights, are as follows:-

	Grade Sn %.	Recovery Cumulative %.
1st pass	25	50
2nd "	12	75
3rd "	6	87
4th "	4	92
Calculated grade:	12% Sn.	

The rougher concentrate could be cleaned by redressing with reduced selector area or by the use of suitable reagents.

Comparison of the effect of the same reagents, on solids adhesion at the selector-pulp interface, with this ore and with the scheelite ore, shown in 5.1, is interesting. Activation of the paraffin with 0.08 gm. oleic acid/l. caused no material change in grade and recovery from neutral conditions. The addition to the pulp of 0.25 gm. sodium silicate/l. prevented adhesion to the selector of all solids (except a small amount of mineral having the appearance of native copper which was identified as haematite with limonite coating (Report No. P.R.C. 24/59)).

Tests showed that a concentration of 2.0 gm. oleic acid/l. was required in the selector to give visibly complete collection of cassiterite and that a concentration of 0.06 gm. sodium silicate/l. (1 lb./ton ore) was too powerful for selective repulsion of the gangue minerals.

The test work was pursued in the direction of promoting selectivity.

Preferential adhesion of cassiterite is preserved when the selector contains oleic acid to the extent (2.0 gm./l.) which gives apparent full recovery in one pass. In the presence of oleic acid, however, there is some sacrifice of the selectivity under neutral conditions.

This lower selectivity is not significantly changed by acid conditions, but is improved, and recovery also is improved, in a weakly alkaline pulp (pH 9). Recovery decreases at pH 10.

Adhesion of quartz and tourmaline, the main gangue minerals, is non-selective under neutral conditions or with oleic acid in various concentrations in the selector under acid conditions, but in an alkaline pulp tourmaline adheres with marked selectivity, especially at pH 10.0. The proportions appear to vary linearly with change in pH value. At pH 9.0 tourmaline and quartz report in the concentrate in substantially equal proportions.

Oleate ion is apparently the effective sorbent for cassiterite and to a lesser degree for tourmaline.

Without conditioning the pulp with repellant agents for the gangue, but with increase in oleic acid concentration, from 0.2 to 2.0 gm./l. at pH 9, to increase recovery, the grade of concentrate decreases from 24% to 8% SnO_2. This is due to the adhesion of tourmaline and quartz in the interface greatly reducing the area available to the less frequent cassiterite particles. Even so, collection of cassiterite is visibly complete if sufficient area is manufactured in breaking the test volume of selector into globules by agitation.

With increase in oleic acid concentration, the force of adhesion is increased for all ore constituents, and for every cassiterite particle there are approximately 40 gangue particles competing in varying degree for the available selector area. As collection of cassiterite increases, due to preferential adhesion, the chances of the remaining free particles progressively diminish. The small globules manufactured from the test volume of selector by agitation become stabilised immediately with solids and are rigidified. This prevents auto-cleaning and thus produces a lower grade concentrate than would be the case if sufficient selector were provided in the treatment of an unconditioned pulp, or as would apply in the continuous phase method.

At this stage it had been determined, preparatory to investigating pulp conditioning for selectivity, that the best recovery of cassiterite could be expected within a pH range of 8.0 to 9.5 with the selector containing 1.0 to 2.0 gm. oleic acid per litre. This is forty times the concentration required for scheelite.

Tests No. 62 to 64 show that a constituent of the demineralised water, in which the tests so far had been made, and of the tap water to a greater extent, consumes hydroxyl ion. The ore does not consume alkali or acid. The constituent is probably organic and responsible for the toxic effect found in testing the water with the control scheelite ore mentioned in 5.1.

The next series of tests, Nos. 61 to 70, therefore, were made in distilled water to preserve ideal conditions. Other changes for this series were as follows:-

The reagent-technique qualitative apparatus was elaborated in an endeavour to permit quantitative determination of results, but was found to be unsuitable because of the degree of agitation involved, and the breaking of the selector phase being dissimilar to practice.

Since the quantity of concentrate produced with this apparatus was too small for assay, attempts were made to assess the concentrate more accurately than by the qualitative method of

(1) vanning, visual split and weighing,

by means of

(2) specific gravity assays, using a pyknometer, and

(3) heavy liquid separation and microscopic examination, to determine percentage cassiterite, quartz and tourmaline.

Both methods (2) and (3) proved unsatisfactory. The results of heavy liquid separation could not be reconciled with the tailing assays, probably because of composite grains.

For the series 61-70, selected tests from the series 31-60 were repeated and significant changes in collection were shown by the use of distilled water instead of demineralised water.

With neutral selector, recovery of cassiterite at 47%, by tailing assay, and calculated grade of concentrate at 29% Sn are not materially altered (the respective values indicated by method (1) above are 50% and 25% Sn), but the proportions of tourmaline and quartz in the concentrate are changed from 20:80 to 60:40.

With selector containing oleic acid, comparable results with recovery at 78% and grade of concentrate at 7.5% Sn were obtained with lower concentration of oleic acid (1.0 gm./l.) with distilled water than with demineralised water (2.0 gm. oleic acid/l.)

The proportions of tourmaline and quartz collected in the concentrates, 60:40, are unaffected by the presence of oleic acid or its concentration, or a change in pH value, which is not the case with demineralised water.

There is evidence that the above effects are caused by organic matter in the demineralised water, and are possibly due to adsorption of amino acids. Later, a wash bottle used for demineralised water had accumulated a bright green organism over a period of about two months. The contents have been bottled for future investigation.

The low grade of the concentrate is due, apart from unconditioned pulp, to the manufacture by the test method of small rigid selector-mineral agglomerates incapable of auto-cleaning. Larger and mobile selector globules in the same pulp charge carry a concentrate of about twice the grade of that carried by immobile agglomerates.

Removal of these small agglomerates from the tailing before assay, for combination with the concentrate, was attempted in this series with a 200 mesh screen in a specially made housing, but the procedure was found to be slow and unsatisfactory.

From tests in which the collection of free cassiterite was visually complete, by sorting in the test cylinders, the actual recoveries determined from tailing assays were 78% and 81%. The difference is thought to be accounted for, apart from unseparated agglomerates, by unsortable low density composite grains in the test size fraction. This is supported by low and unreconcilable results from heavy liquid separation of the concentrates. Composite grains have less chance of adhering to the selector than free cassiterite, especially under the test conditions and in unconditioned pulp.

The size fraction is based on the specific gravity of cassiterite; the size range of cassiterite below 76 microns, therefore, is wider than for quartz and tourmaline, and composite grains would be concentrated in this fraction. This is supported by the size analysis of the minus 200 mesh fraction shown in Table 2 of Section 3, Test Material.

When it became evident, in April, that the elaborated reagent-technique apparatus was unsuitable for quantitative work (for which it was not originally intended), and after a period of experimentation, apparatus was designed for the continuous phase method at laboratory scale which could be changed to pilot scale.

This apparatus involves continual flows in the wash water and selector circuits and of water in the pulp circuit, to speed up testing and provide information from continuous running, especially of masking of the interface by the tap water. Test pulp charges are introduced pneumatically into the pulp circuit and pass through the collecting vessel to a tailing receiver. The concentrate adhereing in the selector-aqueous interface passes through a washing section to a separating vessel in which the concentrate is collected.

The apparatus is designed for pulp charges containing a minimum of 100 gm. of ore at 33% solids, and for a flowrate of 100 ml./min. .

After initial testing of the collecting method, a glass collecting vessel, the washing section and the separating vessel were made. These units were received during May. The collecting vessel, tested with static selector and dyed water, gave satisfactory flow performance over a range 60 to 280 ml./min. from a $\frac{1}{8}$ in. dia. jet, and so requisitions were made, commencing on 10th June, for the ancillary equipment, including pumps, rotameters, etc. .

Testing has shown that a standard rotameter can be converted to indicate the rate of selector flow.

A satisfactory method has been worked out for the determination of oleic acid concentration in liquid paraffin; this is required for control of selector activity with the continuous apparatus.

Two 5 lb. samples of Maranboy ore have been batch ground to provide material in readiness for testing the laboratory apparatus, and also for information in respect to grindability, cassiterite communition and liberation. The aim, attained with the second sample, was a product sizing 80% minus 200 mesh B.S.S. . The minus 200 mesh fraction from the trial grind will be used for mechanical testing of the apparatus.

At 30th June about 50% of the ancillary equipment had been received and assembled.

6. DEMONSTRATION.

By the second week in March means had been devised for demonstrating to senior members of various Sections features of the process characterised in the discontinuous and continuous phase methods to initiate development of the physical application of the process. The following behaviours were demonstrated on 12th March. No definite movement has since been made in this direction.

Discontinuous Phase Method (Scheelite Ore):

Selective adhesion due to minerals' inherent surface energy; increase in the force of mineral-selector adhesion by the use of a molecular link; the formation and nature of mineral-selector agglomerates; levitation of agglomerates; increase in selectivity by conditioning the pulp.

Continuous Phase Method (Scheelite Ore):

The strength of a mineral laden selector-water interface under washing conditions; removal of the interface; grade of concentrate; the supporting strength of the selector medium in relation to coarse mineral grains; the rising velocity of the selector as a continuous phase in water and transport of concentrate at the interface for counter-current washing; the use in apparatus of polar and non-polar material surfaces.

Discontinuous Phase Method (Tin Ore):

The natural selective adhesion of cassiterite under neutral conditions; recovery with activated selector.

Following the demonstration and discussion, Mr. D.C. Madigan contributed Notes on thermodynamic considerations substantiating the physico-chemical theories.

7. DISCUSSION.

Continuation of the test work to determine the efficacy for Maranboy tin ore of the best balance of the same reagents which proved suitable for King Island and Kalgoorlie scheelite ores was interrupted by the necessity of evolving apparatus capable of giving products under similar conditions to practice and in sufficient quantity for accurate assessment.

It is not thought that a non-selective reagent such as oleic acid is necessarily the best for cassiterite, but it is important to determine the effect in the process of such a non-specific reagent on various minerals.

The work ahead entails the finding of a more specific molecular link for cassiterite and compatible repellant agents for the gangue minerals. The next step is the testing of less highly refined oils for the selector medium than B.P. grade liquid paraffin, for economic reasons; but before either of these can be done it is necessary to investigate and remove the cause of the detrimental effect of the Adelaide tap water so that it can be used in the test apparatus.

So far there has been no opportunity to attack the tap water question, but if the offending constituent is organic, as suspected, it is recommended that the advice of the Engineering and Water Supply Department is sought as soon as possible and/or the problem is given to a bio-chemist. It has been mentioned that there is an algae type of growth in demineralised water that could give rise to detrimental protein or amino acids.

The work ahead entails the finding of a more specific molecular

link for cassiterite and compatible repellant agents for the gangue minerals. The next step is the testing of less highly refined oils

Tests show that with tap water sodium silicate is not a useful repellant agent for quartz, but the effect on the control scheelite ore indicates that it could probably be made so by modifying the quartz surface by sorption of ferric ion (see 5.1). This, however, would amount only to one adjustment, and for this particular water.

When the continuous apparatus is completed, test work will be resumed using the reagent-technique apparatus to guide pulp conditioning for testing in the continuous apparatus. This apparatus will give sufficient quantity of products for assay and for determination of the proportions and nature of composite grains in the concentrate and tailing as a guide to grinding for liberation.

Compared with scheelite, the relatively high concentration of oleic acid required to cause adhesion of the coarser cassiterite particles to the discontinuous selector phase should be less in the continuous phase method, because of lower relative velocities of the solid components of the pulp and selector, and consequently satisfactory conditioning of the pulp in this reagent system should be easier. This has been observed experimentally.

It might be found desirable for good selectivity to lower the oleic acid requirement by grinding finer than required for liberation.
