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FLOTATION OF DAVIDITE FROM RADIUM HILL ORE.

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The tests described in this report were made on ore obtained during the initial prospecting and development of Radium Hill. The grades mentioned are no indication of grade of ore reserves of the Radium Hill Project.

The disclosure in this report of information relating to any uranium recovery methods or processes which may be subjects of patent applications is not to be interpreted as a waiver of any patent rights which may be claimable.

Uranium content of samples is reported as pounds of U_3O_8 per long ton.

FLOTATION OF DAVIDITE FROM RADIUM HILL ORE.

S U M M A R Y.

1. This report describes experiments in the flotation of davidite, a uranium bearing mineral, from ore from the Radium Hill mine.

2. The ore veins contain an intergrowth of davidite with iron and titanium oxides, associated with siliceous materials which are predominantly quartz and biotite.

3. Flotation without prior desliming of the pulp became possible when attention was paid to thorough emulsification of the reagents.

4. It is believed that conditions for proper emulsification of reagents are incidentally those which promote most efficient flotation.

GENERAL

Since the beginning of 1950 at least one Metallurgist of the South Australian Department of Mines, has been allocated full time to the testing of flotation methods on ore from Radium Hill. Initially tests were conducted in laboratories at the South Australian School of Mines, and the University of Adelaide. Testing was transferred to the Thebarton laboratories of the S.A. Department of Mines when these were completed in October, 1950.

All the work described herein was carried out on 500 grm charges, prepared by grinding in a stainless steel ball mill, and subjected to flotation in a Fagergren Laboratory Test Machine. Results were later proved in pilot scale equipment in continuous operation, both in Adelaide and at Radium Hill.

Results of the tests were recorded in departmental Progress Reports commenced in April, 1950. Since these have not been generally available, this report is assembled to summarize the results.

The development over three and a half years of the separation of the uranium bearing davidite by flotation has been one of continuous improvement. This is believed to be due to close attention to the emulsification of reagents. The importance of this factor is becoming generally recognised, and is mentioned in recent articles in the technical literature, such as flotation of manganese oxides in Colorado, and uranium lead phosphate in France. The methods used by chemists in formation of oil in water emulsions, adopted by us, have given excellent results, and are probably of wide application in the flotation of other oxide and oxidized minerals.

MINERAL ASSOCIATION

Uraniferous lodes at Radium Hill occur as shear replacements and infillings along fractures developed within a domed anticline in granitized metasediments. The lode material consists of a coarse association of quartz, large books of bronze biotite, and the ilmenite group of minerals, containing davidite.

The davidite, rutile, ilmenite, haematite minerals usually occur together. The segregations may be irregular nut sized concentrations within the silicates, or masses weighing many pounds. The tremendous variation throughout the lodes in the ratios of oxide to silicate minerals is immediately apparent to the eye. There is an even greater complexity of intergrowths and ex-solutions on a microscopic scale within the segregated ilmenite series. Detailed examination by the Departmental Petrologist has shown good evidence of the paragenesis of both siliceous and oxide minerals. It is sufficient to say here that the initial haematite, ilmenite, rutile series was later partially converted to davidite in some parts of the deposit. The mineral content of one ore sample was proportioned as listed below:

Davidite	2.1 per cent
Rutile	4.5
Haematite	0.6
Ilmenite	0.4
Pyrite	0.1
Quartz	40.6
Chlorite Biotite	50.4
Muscovite	0.6
Accessories	0.6

Magnetite was observed in some samples as part of the iron titanium oxide complex, and also as an accessory mineral in the gneiss remnants.

The degree of the intergrowths of the oxide minerals, and their slight association with the siliceous minerals after grinding was apparent from an examination of a flotation concentrate. A concentrate sample was screened and in the size fraction between 0.08 and 0.06 mm contained the minerals listed below.

Davidite	39.9 per cent
Rutile	26.6
Haematite	14.0
Ilmenite	4.5
Magnetite	3.7
Pyrite	trace
Gangue	11.3

The degree of association of each mineral in this fraction was noted as free, binary or complex.

Mineral	Per Cent free	Per Cent Binary	Per Cent Complex.
Davidite	51.5	39.5	9.0
Rutile	39.8	46.0	14.2
Haematite	-	61.0	39.0
Ilmenite	-	65.0	35.0
Magnetite	95.5	-	4.5
Gangue	91.3	3.2	5.5

The variation between samples is confirmed by the different proportions of the oxides in the concentrate listed above in the previous paragraph and those of the ore described.

ADVANTAGES OF FLOTATION.

Fair liberation of the iron and titanium oxides with the davidite is obtained when particles are 2 mm. diameter, leaving the silicate minerals reasonably free of uranium. Early plants at Radium Hill, in 1913 and 1923 had used dry magnetic separation and Wilfley table separation respectively, on material crushed in rolls to about this size. These methods were again checked in the laboratory.

For good magnetic separation the feed must be dry. It was found that four per cent moisture in ore as delivered from the mine was sufficient to prevent clean separation. Many silicate particles contained traces of magnetite large enough to make them report in the magnetic concentrate, causing a lower grade than obtained by gravity separation.

Gravity separation on Jigs and Tables at the appropriate size ranges gave a reasonable grade of concentrate, but poor recovery. Much of the mica and chlorite appeared to have a specific gravity close to 3.0 and interfered with the separation. Clean separation was also made difficult by the presence of some composite oxide/silicate particles. Typical recoveries were of the order of sixty per cent.

Much more complete liberation of the oxide minerals was obtained by grinding particles less than 140 microns diameter. Experimental work on the leaching of uranium from the concentrates indicated that it would be necessary to reduce the oxide minerals to this size to obtain good extraction of the uranium. Two possibilities were explored in the laboratory at this stage.

a. Direct flotation of the ore.

b. Gravity concentration at a coarse size, followed by flotation.

Direct flotation by methods used for haematite, or ilmenite flotation in other countries was considered. It was anticipated that this would be expensive because of the high cost of water and power at Radium Hill, and because oxide flotation would use several pounds of each reagent per ton, compared with the much smaller amounts used in sulphide flotation. It was suspected that the slime fraction would be too valuable to discard.

Preconcentration by gravity methods directed to rejection of a clean tailing appeared to have some merit since it would reduce the bulk of material going forward to the high cost flotation section for final concentration. Despite the interlocking of most oxide particles with silicate particles, it was observed that at the comparatively coarse sizing of two centimetres, at least 70 per cent of the silicate particles contained no oxides. These were ideal conditions for Heavy Media Separation, and test work was immediately successful, giving recoveries in the high nineties on feed between two cm. and one mm. sizing. Seventy per cent by weight of the feed to this section was rejected carrying only five per cent of the uranium.

Flotation tests were therefore directed to samples of the Heavy Media Separation concentrate, and the minus ten mesh portion of the ore not treated in this gravity section. If these fractions were ground to less than 140 microns diameter (70 per cent less than 70 microns) it was possible to obtain a relatively clean oxide concentrate and the final concentrate was also suitable for the subsequent leaching processes adopted for final extraction of the uranium.

Since at this particle size much of the davidite was free it was hoped that differential separation of davidite from iron and titanium oxides might be achieved. Test work in this direction has so far not given any encouraging results.

DEVELOPMENT OF FLOTATION REAGENTS.

1. Initial Testing.

The first reagent used was sodium oleate, tested through a pH. range from 1 to 10. Mineralization of the froth was obtained, but with little selectivity to the oxide minerals. Recoveries were best, but selectivity worst, in the alkaline pulps.

Successful recoveries were first made with "Nutone" which is a mixture of approximately eight per cent sodium naptha sulphonate in a light oil fraction of petroleum. This was the only material locally available similar to "Mahogany soap", as used in the United States. It was necessary to use 60 lb. per ton of feed, added to the ball mill. The pH. of conditioning was varied without significant effect, but a pH. of three to four was most satisfactory for flotation. By adding an additional four pounds per ton of sodium naptha sulphonate it was possible to reduce the Nutone to 18 pounds per ton.

In March 1951 an attempt was made to improve the emulsification of Nutone by the addition of Hydrosol Triple X. The latter reagent contained Potassium oleate, Sulphonated Castor Oil and coal tar acids. This immediately improved recoveries from 70 to 90 per cent, and gave a much greater latitude in reagent addition. Natural pH. was satisfactory and flotation time was reduced.

It was hoped that emulsification of the Nutone would allow reagents to be added to the flotation cell. Stage addition would then be possible with its attendant advantages in full scale operation. Unfortunately tests indicated that addition of reagents to the ball mill gave much better results.

The possibility that perhaps the oleate, or the castor oil was a superior collector to the naptha sulphonate was checked. They were compared separately, and each found inferior to the complete mixture.

2. Emulsification.

Flotation of the oxide minerals is usually considered due to two factors. First, coating of the mineral is obtained in the usual way by adsorption of an anionic active, heteropolar substance such as sodium naptha sulphonate. Second, the contact angle with the air bubbles is increased by the addition of an oil layer to the sulphonate. It was realised that quick collection of the mineral particles with a reasonably small amount of oil could only be obtained if the oil was reduced to droplets comparable in size with the finest mineral particles. Attention was therefore paid to the emulsification of the oil.

Various machines are available for the production of fine oil droplets, but probably none so effective as a ball mill grinding ore. Measurements quoted in technical literature on the chemistry of emulsion s how that droplets down to two microns diameter are formed without much difficulty and give a milk-white product. With droplets below half micron diameter the transmission of light is not affected to a marked degree and the emulsion remains clear. Oils so dispersed are called "soluble". One hundred cc. of oil would supply 19×10^{13} droplets of one micron diameter. Oil addition of 10 lb. per ton of solids in a ball mill pulp of 70 per cent solids, would have droplets at centres of 4.2 microns only, if their average diameter was one micron. This should give efficient contact of oil droplets with the ore particles.

Once the droplets are formed they are stabilized by chemical emulsifiers. Heteropolar water soluble chemicals of similar nature to those used as collectors for the oxide minerals can be used. In fact the collector for the mineral may have the non polar section in the oil surface. Typical emulsifiers in common use are:

Sodium Oleate.
Sulphonated Castor Oil.
Sodium naptha sulphonate.

Droplets of the order of 10 microns diameter are stabilized by the addition of such reagents. Diameters of one to two microns may be readily maintained by the addition of a coupling agent to the emulsifier.

3. Coupling Agents.

These agents consist of heteropolar molecules which are oil soluble. The polar portion, which tends to orient itself away from the oil surface into the water phase, reinforces the surface layer by packing between the polar portions of the emulsifier molecules. The exact nature of this packing is not known, but evidence has been published indicating that the relation is stoichiometric.

Suitable coupling agents are still found largely by trial and error, as it is not always possible to predict which ones will be compatible with the various emulsifiers. Coupling agents in common use are:

Oleic acid.
Napthenic acid.
Commercial cresol.
Pine oil.

The exact role of the oleic acid, as a coupling reagent is determined in part by the pH at which it is used since saponified oleic acid is an emulsifier.

The amount of emulsifier absorbed in the surface of the oil droplets (at one micron diameter) is approximately one per cent of the weight of the oil. More than this must be added to maintain sufficient concentration in the aqueous phase after mineral particles and oil droplets have abstracted reagents by adsorption. This becomes important with dilute emulsions as used in flotation. Amounts found necessary in practice are 10 to 30 grms. emulsifier and 5 to 15 grms. coupling agent per 100 grms. of oil. This would correspond to a ball mill charge as follows:

10 lbs. fuel oil per ton of feed.
2.0 lbs. emulsifier per ton of feed.
1.0 lbs. coupling agent per ton of feed.

4. Multiple Reagents.

If the dilution of an emulsion is to be varied greatly, the use of two emulsifying agents is often advantageous. The practice is therefore applicable to flotation pulps, as concentration of oil droplets is continually varied. A weakly adsorbed reagent of low molecular weight is used to ensure stability of the concentrated emulsion, with a strongly adsorbed reagent of high molecular weight to ensure stability in the diluted system.

Inorganic salts which are strong electrolytes will stabilize the surface layer of the oil droplet in much the same way as a coupling agent. The effect is additive, and if salt is present, the amount of coupling agent must be reduced.

The surface layer of the oil droplets is only stable when the correct balance is achieved between the various components. Too much emulsifier, coupling agent or salt will cause coagulation, and seriously upset

flotation. In tests designed to check requirements of any one reagent these characteristic optima were always very definite.

Flotation was readily achieved provided components in the reagent mix were an emulsifier, or a mixture of two emulsifiers, a coupling agent and petroleum oil (diesel fuel being most convenient). Recoveries using HMS concentrate as feed, were well over 90 per cent. Many mixes were tested in order to find the most economical and after thorough laboratory testing, the three listed were used for flotation in a pilot plant.

1.	Hydrosol Triple X.	(Sulphonated castor oil. Potassium oleate. Cresol).	12 lbs/ton
	Diesel Fuel.		8 " "

Reagent cost per ton 20.0 shillings.

2.	Whitcol	(Sulphonated fish oil)	6 lbs/ton
	Cresylic Acid.		1 "
	Fuel Oil		8 "

Reagent cost per ton 10.0 shillings.

3.	Peltogen	(Sulphonated Whale Oil)	2 lbs/ton.
	Sodium Oleate.		4 "
	Cresylic Acid.		1 "
	Fuel Oil.		8 "

Reagent cost per ton 9.75 shillings.

5. Branched Chain Reagent.

The configuration of molecules adsorbed in bubble surfaces during flotation has received considerable attention in recent technical literature. The use of cresylic acid to hasten adsorption and to strengthen the film is advocated. The advantages of branched chain collectors and unsaturated molecules in spreading the surface films is also described. These studies closely parallel the work of emulsion chemists.

The most efficient collector used to date on a weight basis, is a sulphonated sperm whale oil, marketed as Peltogen. This oil is largely an esterified glyceride, and the figuration of the collector molecule with the sulphuric radicle in the centre of Y-branch is probably the reason for its high efficiency. This is indicated in work of Climax Molybdenum Co. where a sulphonated glyceride was preferred to a sulphated alcohol.

The effectiveness of Peltogen was demonstrated on flotation of the slime fraction of the ore, where recoveries were improved by approximately ten per cent.

5. Unsaturated Reagents.

Flotation tests using various fractions of tall oil for collecting ilmenite, reported from the Finland Institute of Technology, demonstrated the superiority of linoleic or linolenic acid. This is in accordance with use of unsaturated molecules for strengthening surface film, as these acids are less saturated than oleic acid.

The oleic acid portion of the Peltogen mix was changed to linoleic acid. Immediately it was possible to reduce the quantity of this ingredient from 4 to 2 pounds. A search was then commenced for cheap local materials rich in linoleic or linolenic acid. By-products from the refining of linseed and grape seed oil have been found satisfactory. The composition of the fatty acid condensate from linseed oil has the following composition:-

Linolenic acid.	48 per cent.
Linoleic acid.	12 " "
Oleic acid.	12 " "
Saturated acids.	28 " "

The most economical reagent mix established at present uses this fatty acid condensate.

Peltogen	1.5 lbs.	per	ton.
Linseed Fraction	2.0 "	"	"
Cresylic Acid	0.5 "	"	"
Fuel Oil	8.0 "	"	"

Reagent cost per ton 6.75 shillings.

DETAILED RESULTS OF FLOTATION TESTS.

The distribution of Uranium in a sized sample of flotation feed shows a concentration in the finest fraction, emphasizing the importance of the slime portion of the ore.

TABLE No. 1

Screen Analysis of Flotation Feed.

Mesh	Per Cent Weight	lbs. U_3O_8/ton.	Distribution per cent
plus 65	0.5)	4.2	4.6
100	7.5)		
150	14.0	5.4	10.4
200	15.5	6.0	12.8
325	25.5	6.7	23.5
minus 325	37.0	9.6	48.7
Total	100	7.3	100

Flotation with Nutone, (light petroleum oil plus sodium naptha sulphonate) using 40 pounds of reagent per ton of ore, gave most satisfactory results when pH. was taken to approximately 3.5 with sulphuric acid.

TABLE No. 2.

Flotation with Nutone. Variation of pH.

pH.	Feed lbs. U_3O_8/ton.	Concentrate lbs. U_3O_8/ton.	Recovery per cent
2.1	7.6	27.8	34.4
2.6	8.1	30.7	65.4
3.8	8.7	34.9	56.6
5.3	7.2	27.6	33.9
6.8	7.6	26.0	18.4
9.9	7.4	8.9	14.8

The optimum amount of Nutone was determined at 60 lb. per ton. Reagent in excess of this amount rapidly prevented flotation.

TABLE No. 3.

Flotation with Nutone. Variation of Reagent Quantity.

Nutone lbs/ton	Feed lb. U_3O_8/ton.	Concentrate lb. U_3O_8/ton.	Recovery per cent
20	8.1	17.7	7.9
40	7.2	28.2	41.1
60	6.7	26.2	72.6
80	7.2	22.0	68.9
120	7.4	13.0	31.4

The addition of sodium naptha sulphonate to the Nutone allowed a reduction in the total amount of collector required. The following tests were made at approximately pH. 3, using 18 lbs. of Nutone per ton.

TABLE No. 4.

Flotation with Nutone. Addition of Sodium Naptha Sulphonate.

Added Sulphonate lbs/ton.	Feed lbs. U_3O_8/ton	Concentrate lbs. U_3O_8/ton	Recovery per cent
Nil	7.4	25.5	25.1
1	7.6	27.1	66.4
2	8.1	30.2	70.6
4	7.6	31.3	81.2
6	6.5	23.3	60.3
8	8.0	25.8	43.7
16	7.5	20.8	37.9

Hydrosol Triple X was added to Nutone in varying proportions. For the first time heavily laden froth comparable with sulphide flotation was obtained. It was noted that the best results were obtained with pH. near neutral. Hydrosol contains potassium oleate, coal oil fraction containing Tar acids, and sulphonated castor oil. Typical results are given, using only 4.5 lbs. Nutone per ton.

TABLE No. 5.

Flotation with Nutone. Addition of Hydrosol.

Hydrosol lbs/ton.	Feed lbs. U_3O_8/ton	Concentrate lbs. U_3O_8/ton	Recovery per cent.
2	6.7	20.2	50.4
4.5	7.5	25.9	77.3
7	6.5	16.3	89.1
9	7.5	15.6	93.3

Three tests were made using 6 lb. Nutone and 12 lb. Hydrosol per ton to check effect of conditioning period on flotation of HMS sink. In this series some sulphuric acid and lactic acid were also added in attempt to improve the grade of concentrate. In this, and all further tests, natural pH. has been used.

TABLE No. 6

Variation in Conditioning Time

Conditioning	Concentrate lbs. U_3O_8/ton.	Recovery per cent
Cell - 10 minutes	31.8	28.4
Cell - 60 "	28.0	40.0
Ball Mill - 45 minutes	28.2	93.2

The effect of cresylic acid as a coupling agent was checked with potassium oleate (6 lbs/ton) and Fuel oil (4 lbs/ton). Amounts in the order of 1 lb. per ton increased the recovery ten per cent, with some sacrifice in grade of product.

TABLE No. 7

Addition of Coupling Agent.

Cresylic Acid lbs/ton	Feed lbs. U_3O_8/ton	Concentrate lbs. U_3O_8/ton	Recovery per cent
Nil	1.7	5.0	78.7
0.25	1.6	4.7	77.8
0.5	1.8	3.8	83.2
0.75	1.7	4.5	87.7
1.0	1.8	3.1	86.0
1.25	1.7	4.6	87.8

A comparison was made between flotation of ground ore, and flotation of the slime fraction of the ore using a reagent combination which had moderate emulsifying properties (tall oil, fuel oil and sulphuric acid) and a reagent group forming a good emulsion (Peltogen, fuel oil, sodium oleate and cresylic acid). The slime fraction does not respond as readily to flotation as whole ore, but it is not so deleterious to recovery with the thoroughly emulsified reagents. Reagents in each case were added to the ball mill.

TABLE No. 8.

Flotation of Slime.

Reagent	Fraction	Feed lbs. U_3O_8/ ton.	Concentrate lbs. U_3O_8/ ton	Recovery per cent
Tall oil group	Whole ore	9.7	23.7	88.9
	Slime	11.1	15.7	77.1
Peltogen group	Whole ore	10.4	25.4	96.6
	Slime	11.0	17.1	86.0

The slime constitutes about 15 per cent of the ore. It is apparent that in each case the sand fraction of the whole ore is giving excellent flotation results.

If the sand fraction alone is treated by flotation, adding the reagents to the cell for conditioning, the agitation will produce a better emulsion with reagents of the peltogen group, but the recovery will be less than with conditioning in the ball mill.

TABLE No. 9

Flotation of Sand.

Reagent	Feed lbs. U_3O_8/ ton.	Concentrate lbs. U_3O_8/ ton	Recovery per cent.
Tall oil group.	10.2	19.4	60.5
Peltogen group.	10.0	24.2	85.9

Alternative collectors were used in an effort to improve the recovery. A typical comparison is given with low grade feed using 6 lb. Fuel oil, and 2 lbs. cresylic acid per ton.

TABLE No. 10

Variation of Collector.

Collector	Feed lbs/U_3O_8/ton	Concentrate lbs. U_3O_8/ton	Recovery per cent
Whitcol 4 lbs/ton (Sulphonated fish oil)	2.2	7.3	63.3
Sulphonated castor oil 4 lbs/ton	1.8	5.3	76.5
Peltogen 4 lbs/ton (Sulphonated Whale oil)	1.6	5.9	68.4
Hydrosol 14 lbs/ton Sulphonated Castor Oil + Potassium Oleate.	1.8	5.3	76.5
Peltogen (2) + Sodium Oleate (4)	1.7	7.0	79.2

Further variations of collector addition were tested on higher grade feed where the improvement in the tailing would be accented. Peltogen plus sodium oleate, with cresylic acid and fuel oil was tested in many proportions. This proved to be an economical and flexible combination. The sodium oleate was replaced in part by other members of fatty acid group containing linoleic or linolenic acids. Reduced amounts were required and the cost of reagents was considerably lowered. Peltogen (1.5 lbs/ton), cresylic acid (0.5 lbs/ton), and fuel oil (12 lbs/ton) were mixed with further collectors detailed in Table No. 11 to show the more powerful effect of the less saturated compounds.

TABLE No. 11

Various Fatty Acids.

Added Collector.		Feed	Concentrates	Recovery
Sodium Oleate.	6 lbs/ton	10.0	32.0	96.3
Oleic 50%) Linoleic 48%)	4 lbs/ton R721	10.2	38.6	97.5
Oleic 12%) Linoleic 12%) Linolenic 48%)	2 lbs/ton Linseed fats.	10.7	28.4	96.0

DISCUSSION OF RESULTS.

Many of the flotation tests described in this report have been of the tedious and expensive, trial-and-error type. Justification for the work is found in the reduction of reagent costs of 27/6 per ton with the original Nutone mixture to 6/9 per ton with the present carefully emulsified oil.

The multitude of reagent combinations are now falling into a simple pattern which is compatible with recent theories in the physical chemistry of both flotation and emulsions.

Further test work must still be of a trial and error nature, but the direction the investigations must take is defined. Variations in components of the surface films should be made in an attempt to strengthen it. Trial of multi-branched chain collectors, new coupling agents such as glycerol mono-oleate and the addition of other non-ionic compounds is recommended.

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