

Laboratory Flotation Characterisation of a Uranium-bearing Copper ore

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Abstract— as part of a metallurgical investigation to identify factors which may promote undesirable recovery of uranium in a copper concentrator in Australasia, detailed mineralogical analysis was performed on several drill core samples to identify the uranium bearing phases and other problematic species that could interfere with the flotation of copper sulphides. This was undertaken in parallel with laboratory flotation tests of the drill core samples to investigate the relative flotation behaviour of uranium bearing minerals. QEM-SCAN analysis was conducted on the flotation concentrate to establish the forms in which U was recovered. The study found that uraninite (UO₂) and masuyite (Pb[(UO₂)₃O₃(OH)₂].3H₂O) were the major U-bearing minerals, extremely fine grained (average grain size 4µm) and apparently associated with copper sulphides and pyrite. The flotation recovery of uranium minerals was moderate (less than 12% in all samples) but above the expected entrainment levels. This can be ascribed to the intrinsic association with copper bearing sulphides (poor liberation). No naturally hydrophobic minerals such as talc, kerogen, etc were identified in the ore mineralogy to trigger any other flotation mechanisms of uranium. Entrainment appeared significant particularly in soft and lower grade ores.

. (Abstract)

Keywords- Copper ores, process mineralogy, uranium, flotation

1. INTRODUCTION

Uranium in nature occurs as oxides and oxysalts defining their higher chemical affinity for oxygen than for sulphur. Apart from uraninite/pitchblende, the simple uranium oxide mineral (UO₂), uranyl minerals generally occur as expressed in equation (1) [5], [9], [10].



where M = Na, K, Mg, Ca, Ba; Al, Pb, Bi, Fe, Co, Cu, Zn; REE (Y, La, Lanthanides), actinides (Th) and XO₄ = PO₄, AsO₄, VO₄, SO₄, MoO₄, WO₄, CO₃.

In copper ores, uranium often occurs as discrete phases [2], [9] and is not known to replace copper, Cu(II), in the copper mineral lattices, owing to high nominal charge at uranium (U⁴⁺ or U⁶⁺) sites. These uranium minerals are not expected to float with short-chain collectors such as xanthates employed in

copper sulphide mineral flotation. Long-chain non-thiol compounds are reportedly good collectors for uranium minerals. In the Elliot Lake uranium ore in Canada for instance, chelating agents such as cupferron, Kelex 100 and TOPO were found to float uranium with cupferron giving higher recovery and better selectivity [11]. However, a work by Makanza and co-workers [3] reported high recovery of uranium with potassium amyl xanthate in the Witwatersrand gold ore of South Africa. The flotation of the uranium minerals brannerite and uraninite was promoted by association with pyrite and naturally hydrophobic bituminous material known as kerogen and not related to any inherent floatability. In general, unwanted hydrophilic minerals known to report to sulphide minerals concentrate through one or combination of the following mechanisms;

- (i) As composite particles with Cu sulphides (an issue of poor liberation)
- (ii) As composite with sulphides such as pyrite [3], [8]
- (iii) Entrainment [6], [7], [13]
- (iv) Activated by Pb (Pb in uranium minerals as radioactive decay product) or by Cu (Cu²⁺ ions in solution) [3]
- (v) Associated with non-sulphide naturally hydrophobic minerals e.g. kerogen [3]

In a particular copper operation in Australasia, uranium occurs in sub-economic levels in the ore (less than 100 ppm U). The recovery of uranium in the copper concentrate is undesirable owing to smelter penalty concerns. This paper presents work carried out to identify the factors which may contribute to uranium recovery in the concentrate by means of detailed mineralogical analysis and metallurgical flotation tests on drill core samples obtained from seven different ore zones. The ore zones were defined by copper and gold grades with unequal distribution of uranium. The specific objectives of the study were to identify the major uranium bearing phases, the distribution of uranium across size ranges relatively to copper and association characteristics of uranium, particularly with sulphide minerals and other floatable species which may have the potential to trigger uranium recovery. Ultimately, we aimed to establish the likely mechanisms that could promote uranium enrichment in the concentrate.

I. MATERIALS AND METHODS

A. Materials

1) Drill Core Samples

TABLE I. HEAD ASSAY

Grade	ORE TYPE						
	RRG4	RG8	RGY1	RR7	RGW1	SYW1	RY1
Cu (%)	2.4	1.3	2.1	1.0	0.5	0.2	0.03
U (ppm)	49	62	88	59	45	32	11

30 kg each of crushed drill core samples from seven ore zones were received from the mine. The nominal head grades of the samples are provided in Table 1. Drill core samples RRG4, RG8, RGY1 and RR7 were from high grade copper zones, SGW1 from low-grade zone and samples SYW1 and RY1 were from gold-only ore zones. Out of these samples, RGY1 was high in uranium (88 ppm U) and low grade ore SGW1 was low in uranium (45 ppm U).

A representative fraction of each drill core (2 kg) was split out for mineralogical analysis and head assay whilst the rest was split into 500g charges for batch flotation tests.

2) Reagents

Flotation reagents employed in this test were sodium ethyl xanthate (SEX) collector and methyl isobutyl carbinol (MIBC) frother, as recommended by the mine. Lime was used to adjust pH.

B. Methods

1) Sizing

Sizing was performed using a combination of 20µm sieve, Warman Cyclosizer and pre-cyclone for splitting out the -8µm fraction.

2) Quantitative analyses by X-ray Diffractometer (QXRD)

Phase identification of ores in various size fractions was performed using the Rietveld QXRD technique. The XRD traces were obtained from 5° to 90° using CuKα radiation. The step size was 0.02° 2θ. Sieve+ 2011 software and International Centre for Diffraction Data’s PDF-4/Mineral Database were used to identify the minerals from the XRD traces. Quantification of the data was done using Siroquant software. The on-line crystallography open database (COD) was accessed for crystallographic data for the uranium mineral masuyite as this phase was not present within the Siroquant database. SiPhase was used to create an “hkl” file for masuyite so it could be quantified using Siroquant.

3) QEM-SCAN Analysis

QEM-Scan analysis was performed on a selected flotation concentrate. Particle mineralogical analysis (PMA) was used to define the modal mineralogy, including liberation characteristics, mineral associations, grain size estimation, for copper sulphides and other major phases (>1000ppm). For uranium, both PMA and SMS (specific mineralogical search) was employed because of their trace proportion (<1000ppm) in the sample.

4) Batch Flotation

A series of batch flotation tests was performed separately on each ore type under identical conditions in a 2L Agitair cell. Test conditions such as agitation (600 rpm), aeration (6 ml/min) and collector dosage (50 ppm) were predetermined.

The flotation conditions used throughout the test are summarized in Table 2.

TABLE II. LABORATORY FLOTATION CONDITION EMPLOYED

pH	Agitation (rpm)	Aeration (mL/min)	SEX dosage (ppm)	MIBC dosage (ppm)	P(80) size (µm)	Froth Depth (cm)
7.5	600	6	50	30	125	3

The concentrates were collected at 1, 3 and 5 minutes to give a total flotation time of 9 minutes. Each incremental concentrate was sized on 20µm sieve and the sized fractions analyzed for Cu, Au, U, Fe, and S. The total water recovered, including wash water, was recorded for entrainment calculations.

II. RESULTS

A. Modal Mineralogy

The composition of the 7 different drill core samples as defined by Rietveld QXRD is shown in Fig.1. The major copper minerals in all ore samples in the order of abundance are bornite/djurleite, chalcocite/digenite/covelite and chalcopyrite. Gangue mineralization is dominated by hematite, quartz and muscovite followed by chlorite. The main uranium bearing phases identified were uraninite (UO₂) and masuyite (Pb[(UO₂)₃O₃(OH)₂]·3H₂O).

Uraninite is a primary mineral while masuyite is weathered product of uraninite and is expected to be found along the altered and oxidized zones. According to Fig.1, masuyite is found in most of the copper bearing ores (RRG4, RG8 and RGY1) which are dominated by chalcocite and bornite, secondary copper minerals. No naturally hydrophobic non-sulphide minerals such as talc or, kerogen were identified by XRD in all ore types studied.

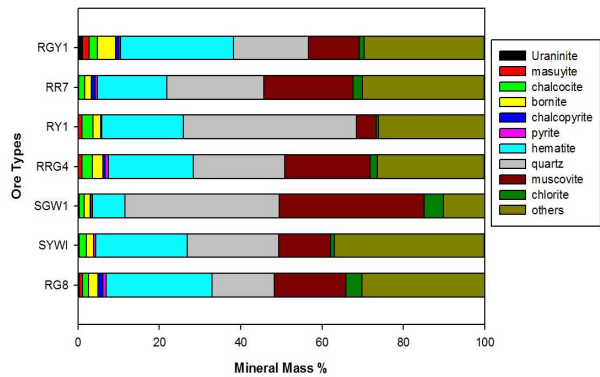


Figure 1. Modal Mineralogy of each ore type as defined by QXRD

Apparently, the gangue minerals are coarser grained compared to the copper sulphides, except for muscovite which is essentially fine grained (Fig.2). For instance, in the drill core sample SGW1, about 45 w/w % of muscovite (KAl₂(Si₃Al)O₁₀(OH,F)₂) is concentrated in the -8µm range. In flotation, unselective recovery of such ultra-fine muscovite is highly possible [6], [13] which can not only dilute the

concentrate grade but also increase the level of another penalty element, fluorine, in the concentrate [7].

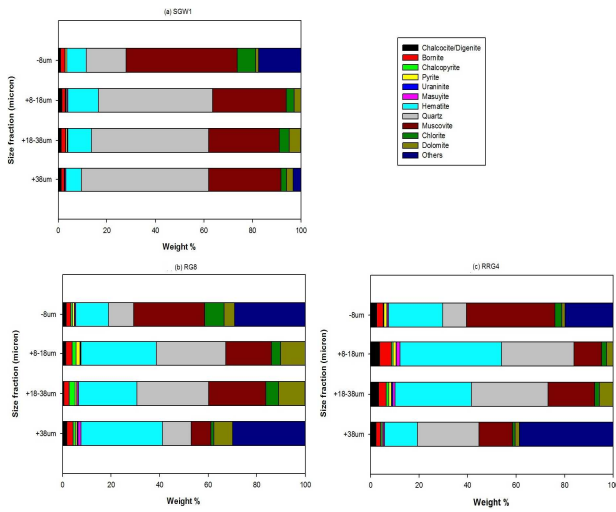


Figure 2. Distribution of minerals by size class in selective ore types as defined by QXRD

B. Association and Distribution of Uranium minerals

Trace elements such as uranium cannot be accurately quantified by QXRD, with a detection limit of 2000ppm [1]. Instead ICP-MS was employed to determine the concentration of uranium in each ore type by size class. The result is depicted in Fig.3. Uranium is concentrated mainly in the copper ores compared to the gold ores (RY1 and SYW1) which are marginally low, indicating uranium is less associated with gold. Of the copper rich ore samples, uranium levels are high in RGY1 with moderate amounts in RG8 and RR7. RRG4 is the only high grade ore fairly low in uranium, similarly with low grade ore, SGW1.

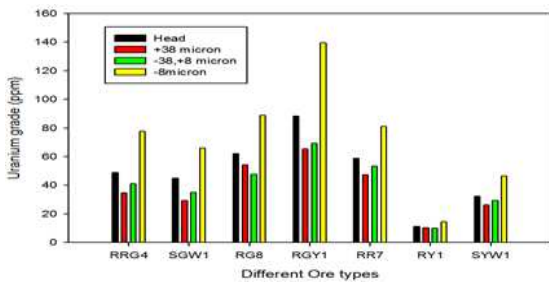


Figure 3. Concentration of uranium in the different drilled core samples studied by size class

Interestingly, uranium is fine grained, concentrating highly in the $-8\mu\text{m}$ range in all samples studied, averaging more than 73 ppm U. In the coarser range, U is less concentrated, 41 ppm in $+8-38\mu\text{m}$ and 38 ppm in the $+38\mu\text{m}$ size range. The distribution of uranium relative to copper is provided in Table 3. Relatively, copper is distributed mainly in the coarser ranges, with less than 20% in the fine ($-8\mu\text{m}$)

where uranium distribution is about 45% in the $-8\mu\text{m}$ fraction on average. Such mineralogical occurrence will present a challenge in sufficiently liberating the unwanted uranium minerals from the copper sulphides.

TABLE III. DISTRIBUTION OF COPPER AND URANIUM BY SIZE CLASS

Ore Type	Cu and U distribution per size class (%)							
	+38 μm		+8-38 μm		-8 μm		Total	
	U	Cu	U	Cu	U	Cu	U	Cu
SGW1	20	26	25	55	55	19	100	100
RGY1	25	39	29	49	46	12	100	100
RRG4	26	38	30	52	44	10	100	100
RG8	33	62	26	28	41	11	100	100
RR7	31	34	30	54	39	11	100	100

C. Metallurgical flotation characterisation

The different samples were floated under identical conditions to assess which ore type(s) contribute to high uranium grade in the concentrate. In order to identify the nature of the uranium bearing particles recovered, two distinct concentrates were collected. The concentrate collected in the first 2 minutes was termed Con 1 and the second concentrate collected after 7 minutes was Con 2. These concentrates were then sized into $+20\mu\text{m}$ and $-20\mu\text{m}$ fractions and chemically analysed. The result is shown in Fig.4. In general, uranium levels in concentrates of gold only ores, RY1 and SYW1 are low (less than 50 ppm U) compared to the copper ores, indicating uranium recovery is linked to copper sulphides recovery. Of the copper ores, concentrates of RGY1 are highly enriched in uranium, quite remarkably in the $-20\mu\text{m}$ range in concentrate 2 (200 ppm U). Almost similar trend is observed in other copper ores although uranium levels are moderate, less than 150 ppm. Uranium grade is generally higher in concentrate 2, and in the $-20\mu\text{m}$ fraction. This highlights uranium is in a fast floating as well as in a more fine slower floating form.

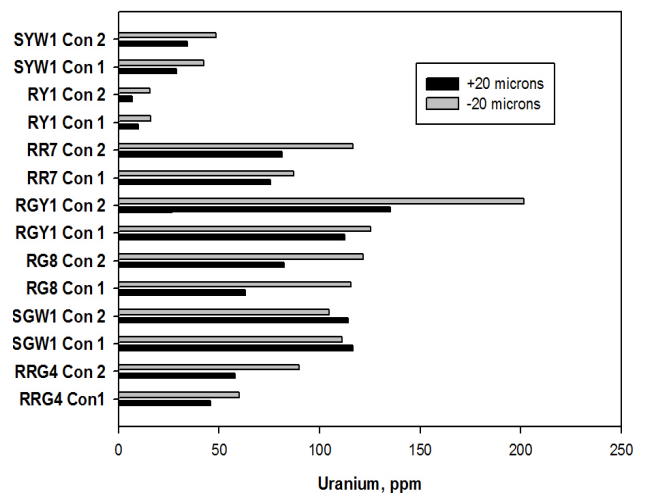


Figure 4. Comparison of uranium concentration in rougher and scavenger concentrates by size for each ore type

TABLE IV. LIBERATION CHARACTERISTICS OF URANIUM AS DEFINED BY QEM-SCAN

Mineral status	Mass %		
	+20	-20/+8	-8
Size (um)			
Liberated	0	43	39
U-Cu sulphides binary	18	26	33
U-Pyrite binary	0	0.3	0
U-Fe oxide binary	4	0	0
U-Silicates binary	1	0	0
U-Cu oxides binary	0	0	0
U-micas binary	0	7	2
Complex(mainly sulphide complex)	77	23	25
Total	100	100	100

The liberation analysis of the concentrate as defined by QEM-SCAN is shown in Table 4. In the -20µm range, significant number of liberated uranium particles were recovered, which are the fines recovered likely via entrainment [6], [13]. The observed increase in concentrate uranium grades (Fig.4) is possibly caused by these liberated uranium particles. Apart from the liberated particles, those uranium phases recovered in association with mica (muscovite) and hydrophilic iron oxide (Fig.5a) are also by entrainment.

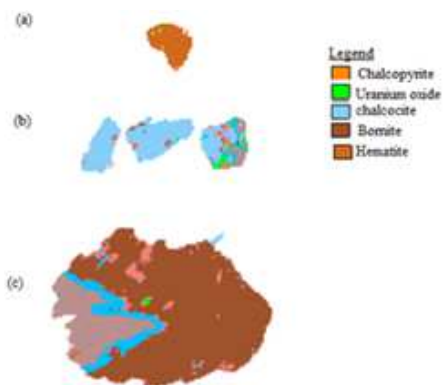


Figure 5. Texture of uranium bearing +20um particles (a) U-hematite binary (b) U-Cu sulphides (c) complex

The fast floating uranium species are undoubtedly those mineralogically associated with copper sulphides. Mineral texture of some copper particles containing uranium is shown in Fig 5 (b and c). The major phases are bornite and chalcocite, both in bulk and in peripheral exposure whilst uranium is fully locked. Such particles are expected to be highly hydrophobic, and float quickly.

D. Recovery of Uranium

In terms of overall uranium recovery, this is low in all drill core samples tested. The maximum is only 12% in the soft and low grade ore, SGW1. This implies the majority of the uranium bearing particles were liberated from the floatable sulphides. Figure 6 depicts the recovery of copper (Fig.6a) and uranium (Fig.6b). The ore is easily floatable, with over 50% copper recovered in the first 2 minutes, in all ores.

In order to determine the fraction recovered due to middling with copper sulphides (via true flotation), F_T , the recovery of uranium via entrainment, E_R , during the flotation test was calculated using method by Ross [12], given in equation (2).

$$E_R(t) = X(t) \times R_W(t) \times M(t) \quad (2)$$

where $X(t)$ is the entrainment factor and $R_W(t)$ is the rate of water recovery at time t (min^{-1}) and $M(t)$ is the mass of mineral in flotation cell at time, t . The recovery by entrainment was then subtracted from overall recovery, O_R at time t (equation 3).

$$F_T(t) = O_R(t) - E_R(t) \quad (3)$$

Where $O_R(t)$ is equal to rate of uranium recovery in the concentrate (min^{-1}).

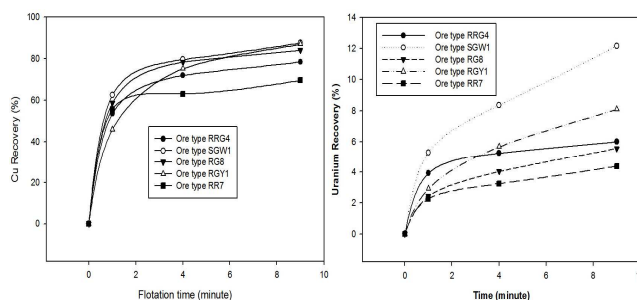


Figure 6. Recovery of (a) copper and (b) uranium in the various drill core samples studied

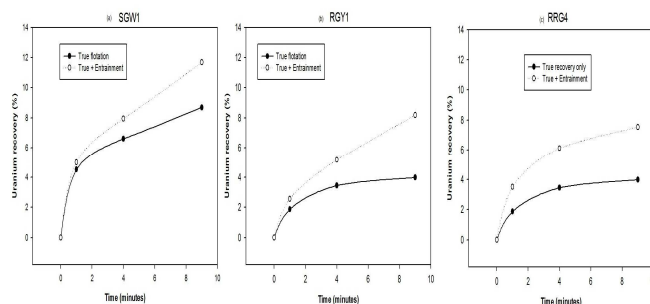


Figure 7. Relative uranium recoveries in (a) soft ore SGW1 (b) RGY1 and (c) RRG4

Selected plots for ore samples SGW1, RGY1 and RRG4 which gave high recovery of both copper and uranium is shown in Fig.7. Clearly, some uranium was recovered via true flotation due to association with copper sulphides. For instance, in the drill core sample SGW1 (Fig.7a), uranium recovered via true flotation is approximately 9% whilst by entrainment is 4% U. Similarly, in samples RGY1 (Fig.7b) and RRG4 (Fig.7c), uranium recovered through true flotation is 4% and 3% U respectively. Overall, equal contribution of liberation and entrainment is observed, elucidating these two mechanisms are equally significant. Addressing either one or both of the factors would result in uranium reduction.

III. DISCUSSION

In the ore investigated, uranium is occurring mainly as uraninite and masuyite, which do not exhibit inherent floatability with sodium ethyl xanthate [8], [11], which is the flotation collector employed at the copper mine. In addition, no evidence of association with naturally hydrophobic non-sulphide minerals such as talc or kerogen was found, which could trigger natural flotation of these uranium minerals [3]. However, at the nominal grind size of P80 of 125 μ m, liberation presents a challenge in this copper mine, owing to the fine grained mineralisation of uranium coupled with intrinsic association with copper sulphides. In this study, approximately 60% of the uranium reporting to the concentrate was recovered due to such mineralogical complexity. Finer grinding is the only option to liberate the unwanted uranium minerals from the valuable copper sulphides. Grinding finer, however, will increase entrainment [4], [13], which is already an equally important factor. The overall recovery of uranium in all drill core samples studied was low, less than 12%, but the concentrate grades were high. For instance, in the drill core sample, RGY1, the concentrate 2 grade was 200 ppm U, a large up-grade from 88 ppm U in the feed. It was found that such enrichment was 50% due to entrainment of fine liberated uranium particles. This implies that minimizing entrainment is critically important. Other factors such as inadvertent activation of uranium by copper ions in solution or lead (Pb²⁺) in the mineral lattice [3] were assumed to be minimal and not pursued further in this study.

CONCLUSIONS

In conclusion, uraninite and masuyite are the major uranium minerals, essentially fine grained, in the ores studied. Over 40% of the uranium is distributed in the -8 μ m fractions compared with copper, which is concentrated mainly in the +8-20 μ m range. Uranium is concentrated mainly in the copper ore zones, with only marginal levels in the gold-only ores.

Poor liberation (due to association with copper sulphides) and entrainment are the major factors identified, which should contribute to uranium recovery in the concentrate. In this study, approximately 60% of the total uranium was recovered due to association with copper sulphides whilst 40% was via entrainment. Minimizing entrainment of liberated fine uranium particles is crucial to reduce concentrate uranium grade. Strategies such as effective froth washing and careful consideration of flotation cell hydrodynamics would be required to optimize fine U rejection.

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