SOME ASPECTS OF LABORATORY FLOTATION OF Co-Cu MINERALS FROM MIXED OXIDE ORES

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Introduction

Copper and cobalt oxide mineral deposits formed by the atmospheric weathering of near surface sulphide deposits are commonplace in the Democratic Republic of Congo. The most common route for the extraction of these metals is a hydrometallurgical one in which the base metal oxides are dissolved in sulphuric acid and then concentrated further by solvent extraction. However, as many of these deposits are relatively low grade (i.e. 0.5-1.8%Co and 2-4% Cu) and can also contain large amounts of acid consuming gangue minerals (i.e. dolomitic, micaeous, and/or siliceous), the hydrometallurgical route becomes uneconomic due to the excessive acid leaching costs. Some means of pre-concentration ahead of leaching is then desirable to improve the process economics. Apart from the small scale mining (Pan. Afr. News Agency, 2000) handpicking, although not easy, oxide concentration by flotation has been suggested. For the flotation process, the two most common approaches are controlled potential sulphidisation (CPS) and the fatty acid flotation method. The preferred method is dictated by the nature of the mineral makeup of the gangue. Being secondary deposits, the gangue associated with these ores is often complex and can play a significant role in the overall flotation efficiency. Laboratory flotation experience gained from the testing of a number of different ores of this type has revealed that it is not possible to prescribe a set method for the flotation of various ore types. Each ore needs to be analysed very carefully before and after laboratory flotation on an individual basis in order to arrive at an acceptable flotation technique

Laboratory flotation testwork was carried out on three different samples from the DRC in attempts to isolate some of the more important variables affecting the flotation of copper and cobalt oxide minerals from these weathered deposits. This paper describes some early results achieved and experiences gained with these different ores ahead of a more detailed flotation test program which will follow in the near future on receipt of a significant quantity of a more representative sample. Controlled Potential Sulphidisation (CPS) was used in an attempt to achieve acceptable recoveries of both copper and cobalt.

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Experimental

Materials

A number of cobalt-copper oxide ore samples were obtained from the DRC for the purpose of investigating the flotation response of particularly cobalt oxide minerals under sulphidising conditions. The origin of two of these initial samples was unknown. The samples consisted of lumps of presumably handpicked large ore particles including very little fines and were in no way representative of a particular deposit. It was nevertheless decided to proceed with the testwork using two of the more suitable samples, based on their cobalt and copper values to gain familiarisation with the flotation technique ahead of the arrival of a bulk sample which was to be delivered at a later date.

The quantities of the initial samples received were limited and this meant that they were exhausted before full optimisation could be achieved. Two of these early samples received are referred to as DTB 1 and DTB 3. The DTB 3 ore with cobalt and copper values of 4% and 13 % respectively could not be regarded as typical flotation feed stock but was all that was available at the time. It was thought that it could be used to evaluate some basic principles such as the use of Controlled Potential Sulphidisation (CPS). Valuable information was gained in the interim about the behaviour of these ores under the flotation conditions tested . Finally, a few initial tests have been done on a large representative sample received from Gecamines, labelled GS. Unlike previous samples this ore is fine, 50% -75μ but it has been confirmed that it is Run of Mine ore.

Methodology

The first tow samples were crushed to – 5 mm using laboratory jaw and cone crushers and then thoroughly mixed and split using a rotary splitter into approximately 500gram portions. The initial flotation test mass of 1000grams solids was reduced to 500 grams in an attempt to improve flotation results and to enable a greater number of tests to be conducted on the limited quantities available.

Grinding tests were carried out to achieve a fineness of approximately 70 per cent minus 75 microns. Grinding times were different for different samples and depended on the ore fineness, as received, as well as the ore hardness. The large bulk GS sample was approximately 50% passing 75microns, as received and required only a short polishing grind. Milling ahead of flotation was done using a laboratory rod mill at a pulp density of 60 % solids.

The pH was measured before flotation and adjusted to approximately 9.5 with calcium hydroxide. Pulp temperature was controlled in the range 23 to 28^{0}C in the flotation cell. A Wemco flotation cell of 2,5 litre volume was used with the rotor set at 1200rpm. Induced air was used in all cases. Sodium sulphide was used as the sulphidising agent and was added as a solution after adjustment of the pH of the solution to approximately 11.8 by the addition of dilute sulphuric acid. This was felt necessary to prevent the pH

rising to above 11 or more during the test with the addition of the highly alkaline sulphide solution. The natural pH of the sample was about 9. Potassium amyl xanthate collector and Dowfroth were used for all tests. Ammonium sulphate was also added to all tests as suggested by Bastin (1978). Sodium sulphide was added manually to control the potential in the flotation cell before a potential controller was developed for this purpose. The difference between manual and automatic potential control was marginal as the assistant's expertise improved with practice. The controller, however, permitted greater care to be exercised during the tests and more frequent readings of pH, temperatures etc to be taken.

Reagent conditions were varied from test to test in an attempt to achieve improved recovery results. For example PAX was increased in stages from a single 80g/t per ton dose to about 200g/t per ton, added in stages prior to each concentrate removal. Seven rougher concentrates were taken for each test and flotation times varied from three minutes for RC1 to RC3 to 4,5,6 and 7 minutes for the remaining concentrates RC4, RC5, RC6 and RC7. In more recent tests, 300g/t per ton of sodium silicate depressant were added in an attempt to limit the impact of the ultrafines. Head grades were back calculated from rougher concentrates, feed and tailings sample values and masses.

RESULTS AND DISCUSSION

DTB 1 Ore Type. (1.0% Cobalt, 4.1% Copper).

Selected large particles of the ore type were examined as hand specimens and subsequently thin sections were prepared for examination under the polarising microscope. In hand specimen it was possible to identify quartz, calcite/dolomite, heterogenite, limonite , malachite and chrysocolla. The positive identification of heterogenite can only be confirmed by XRD analysis. This has yet to be achieved. In hand specimen it was assumed to be present as the black, often amorphous mineral seen as coatings and veinlets on and around other crystalline phases. In thin section the ore appears as a fine grained quartzite rock with a layered structure indicating a sedimentary origin which was later exposed to thermal metamorphism. An opaque oxide black in colour is tentatively identified as heterogenite. This occurs as fine irregular grains within the quartz layers. Malachite is also seen to be present as secondary infillings through the bedding planes. Chrysocolla occurs as discrete grains and also as coatings and veinlets similar to the malachite.

Flotation Conditions.

The test below was conducted using manually controlled potential sulphidisation. Potassium amyl xanthate collector,80g/t, ammonium sulphate 1000g/t,and Dowfroth 200 frother 20g/t were added. The potential was controlled at approximately – 500 mv during the the sulphidisation conditioning stages. 10kg/t of 30% Na_2S was added in total as a solid in amounts 6kg/t,2kg/t,0.5kg/t,0.5kg/t,0.25kg/t,0.25kg/t,0.25kg/t, and 0.25kg/t

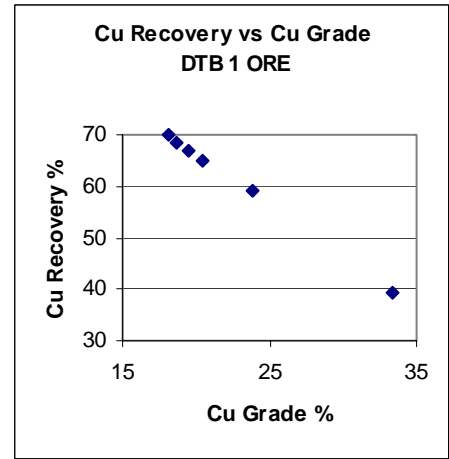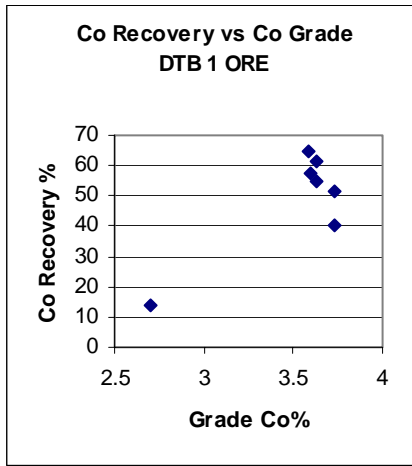before each conditioning stage. A few drops of dieseline were added at three stages during the test.

Figure 1: Co Recovery% vs Co%Grade   **Figure 2:** Cu Recovery % vs Cu%Grade

The RC 1 concentrate value for cobalt for this ore was invariably lower than the second and third etc concentrate values for repeat tests indicating an initial sluggishness of the cobalt minerals to flotation. This was in complete contrast to the behaviour of the copper minerals which displayed a more normal flotation response. The above results were achieved in a total rougher concentrate mass of 17%. The cobalt grades of RC 7 were invariably highest for all tests.
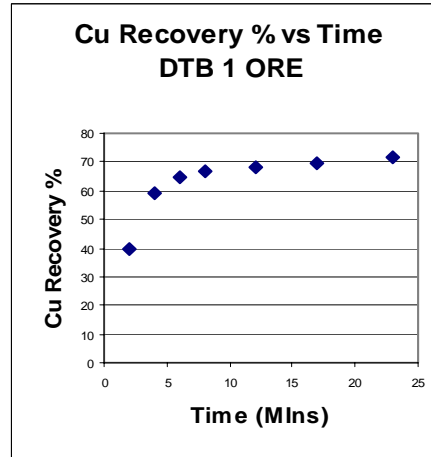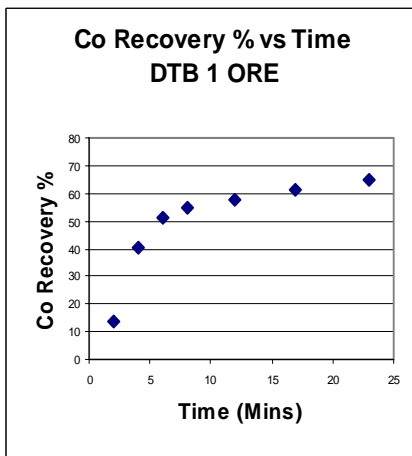
Figure 3   **Co Recovery% vs Time**   **Figure 4** Cu Recovery vs Time

This is further supported by the rate graphs 3 and 4 which also exhibit a slight point of inflection between RC 6 and RC 7 on the cobalt recovery/time graph. This is not

noticeable on the equivalent copper graph which flattens out in the normal manner towards the end of the test.   This could have been due to the fact that the conditions were near optimum for the copper minerals but not for the cobalt minerals and as a result the copper minerals tended to crowd out the cobalt minerals.

 It is also possible that the cobalt is present in two forms of heterogenite , an amorphous and crystalline form each displaying a different flotation response. This became more evident in later testwork on DTB 3. These results indicate a promising start but since the prime objective was the flotation of oxidised cobalt minerals , further tests were done attempting to improve the rate of cobalt flotation and recovery while keeping the concentrate mass within reasonable limits.However, this was not successful due to an inability to isolate the more critical flotation variables with the small amount of sample available.

In general these results were acceptable from a concentration ratio and overall recovery standpoint. The feed was upgraded by a factor of 3.6 for cobalt and 4.2 for copper. This trend of two detectably different cobalt mineral flotation responses was noticeable with DTB 3 ore as well as seen below in Figures 7 and 8. In general this ore appeared to be particularly sensitive to the sulphidisation potential (Jones and Woodcock 1978) and a decision was then taken to develop an automatic system to monitor and control millivolt potentials at predetermined levels.

DTB 3 Ore Type (4% Cobalt, 13% Copper).

In hand specimen, the rocks were very varied in appearance. Some low density particles containing micaceous minerals with interstitial malachite and chrysocolla were observed. Again a fine layered structure is noted in thin section. Fine accumulations of chert and muscovite occur together with the black heterogenite ? mineral. The heterogenite appears to be secondary in nature.cutting through the rock. The heterogenite also occurs within the botryoidal malachite structure together with limonite.

Flotation Conditions.
These were much the same as for the DTB 1 but with sodium sulphide added as a solution. This enabled slightly better control of the potential during sulphidisation conditioning. The recoveries were satisfactory at 71% and 85% . However, what was heartening was that in Graph 5 the Grade/Recovery curve for cobalt was with one exception a "normal"shape while this time the one for copper showed an initial low grade. This reflects the problems of optimally sulphidising high grade ores. As expected the cobalt and copper was only upgraded by a factor of 1.5 and 1.6 and the rougher mass was 51%.
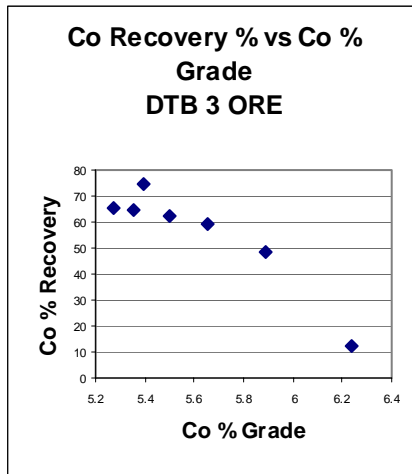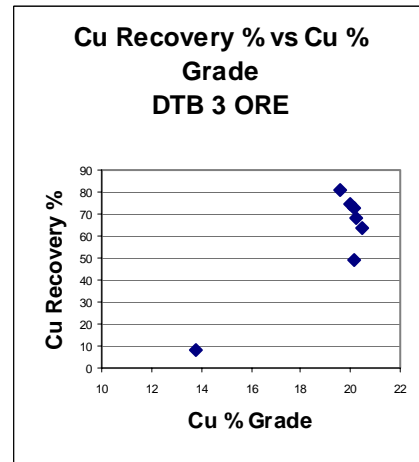
Figure 5 Co Recovery% vs Co% Grade
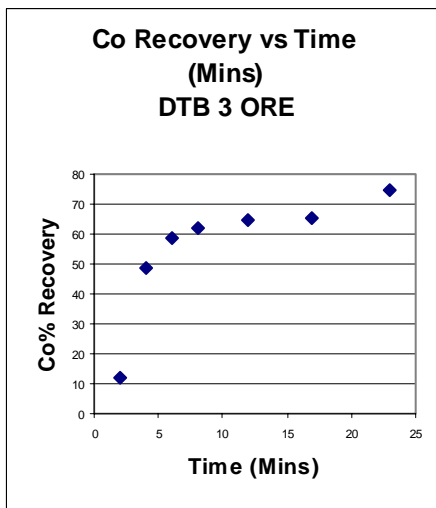

Figure 6 Cu Recovery% vs Cu% Grade

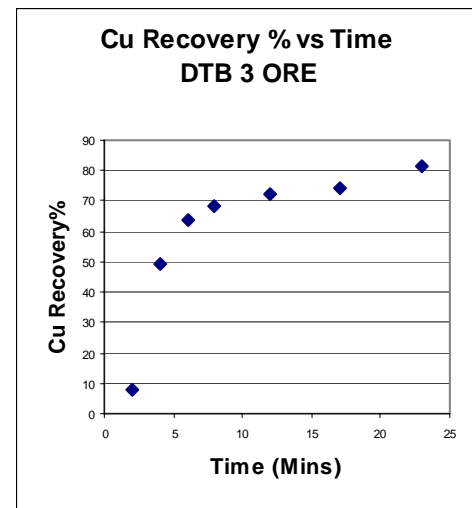**Figure 7** Co Recovery % vs Time

Figure 8 Cu Recovery %vsTime

 A much richer ore sample which would not normally be regarded as a
suitable flotation feed stock..

 The interesting feature of the point of inflection in the cobalt recovery versus time graph
, Graph 7 is again apparent, even more prominently than in the DTB 1 test, Graph 3. It is
also apparent that that the rates of recovery of copper and cobalt are now similar in the
initial stages of flotation. An earlier statistical microscopic study conducted by Prof. J. de
Cuyper (1979) on the flotation tails and concentrates obtained from a sulphidising float of
a cobalt oxide ore suggested that the amorphous varieties of heterogenite floated
preferentially at the beginning of the flotation and that only 3% of the crystalline varieties
were present in the initial concentrate as crystallised oxides. The tailings contained a
much higher proportion of these varieties. In the particular test above,however, the
copper also demonstrates this phenomenon in the rate curve probably caused by the

abundance of floatable copper minerals in the ore which tend to be crowded out in the early rougher stages ?

43 GS Ore Type(1% Cobalt , 1% Copper)

The ore as received was fine, 52% -75µ and did not allow hand specimen examination. It was , however, possible to identify a high proportion of a micaceous mineral in the as received ore. In contrast to DTB 3 the grades for this sample are low and it is doubtful whether they would be economically treatable even given their natural fine particle sizes.

Flotation Conditions

Because of the fineness of the ore 300g/t of Sodium Silicate dispersant/depressant was added to the float for this ore. Only frother and depressant were added for RC1 and RC 2 concentrates in an attempt to float off the mica before the metal oxide minerals. Sulphidisation was implemented after RC 2. Ammonium sulphate 1000g/t and potassium amyl xanthate 80g/t were also only added after RC 2.
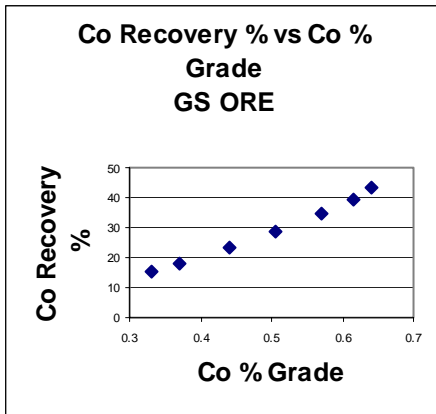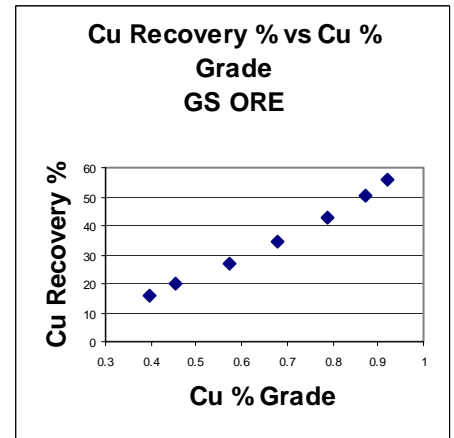
Figure 9 Co Recovery%vsCo%Grade   **Figure 10** Cu Recovery%vsCu%Grade

The GS ore results are substantially different to the DTB1 and DTB 3 results due to the naturally floating mica mineral which dilutes the grade of the first few concentrates. This together with the relatively low copper and cobalt mineral contents, results in the unusual situation where the grade increases as the recovery increases.
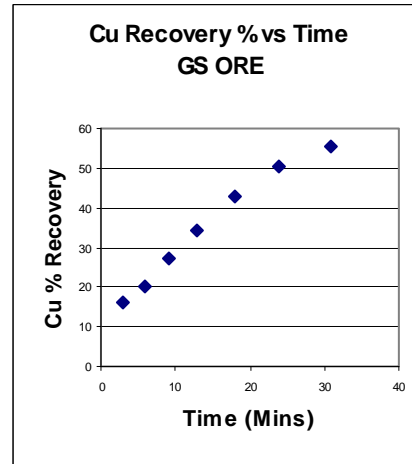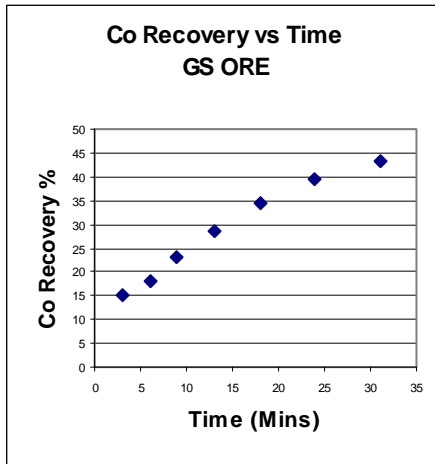
Figure 11 Co Recovery% vs Time   **Figure 12** Cu Recovery % vsTime

The initial two concentrates RC1 and RC2 were very rich in mica and contained only small amounts of copper and cobalt, 18% of the cobalt and 20% of the copper in the feed. After mica removal , 85% of the cobalt and 84% of the copper were recovered in 55 % of the feed mass. The difference in grades of cobalt and copper from the first two concentrates RC1 and RC2 in which the mica is floated to the second stage concentrates RC3 etc in which the cobalt and copper is targeted, are very significant and are shown in Table 1 below.

Table 1: Flotation Results on GS sample

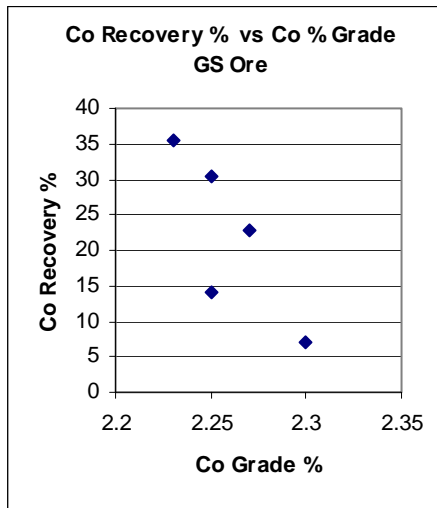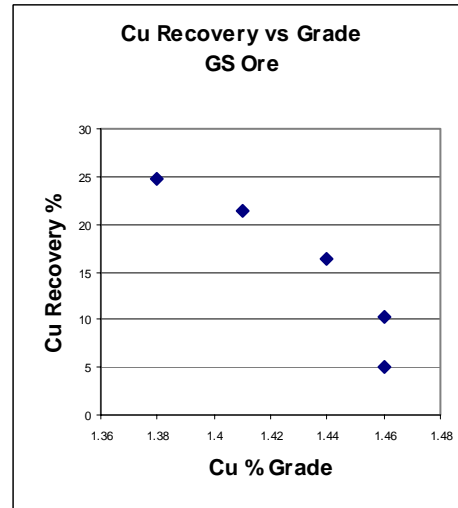| Rougher Concentrate	Mass %	Fractional GradeCo %	Fractional GradeCu %	Fractional Co Recovery %	Fractional Cu Recovery %
RC 1	**44.8**	**0.33**	**0.40**	**15.02**	**16.14**
RC 2	4.0	**0.80**	**1.10**	3.24	3.99
RC 3	3.4	1.46	2.25	5.00	6.95
RC 4	3.6	1.46	2.22	5.31	7.26
RC 5	4.2	1.41	2.26	5.96	8.60
RC 6	3.8	1.32	2.18	5.07	7.51
RC 7	2.8	1.24	2.05	3.49	5.22

Figure 13 Co Recovery vs Grade

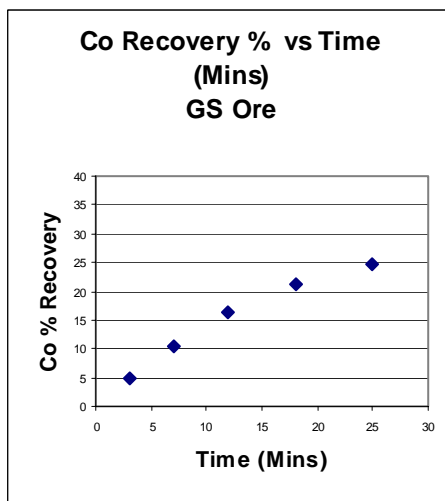**Figure 14** Cu Recovery vs Grade

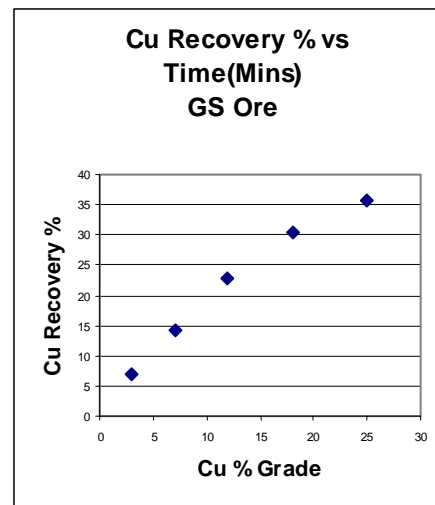**Figure 15** Co Recovery vs Time

Figure 16 Cu Recovery vs Time

After excluding the RC 1 and RC 2 mica concentrates for the GS ore and plotting the remaining concentrates ie RC 3 to RC 7, refer to Tables in Appendices, grade/recovery and flotation rate curves are obtained which are more normal in shape. Neither rate curve, however, displays an appreciable flattening off of the graph slopes indicating that the metal recovery conditions were not ideal and could hopefully be increased. A factor in this is that the feed pulp density is low because only 0.5kg is used per test. Around 50% of the mass is removed with the mica leaving a very low pulp density in the second part of the float. This will reduce the flotation kinetics and consideration may have to be given to testing a larger feed mass of say 1kg. The possible removal of the mica by classification ahead of flotation would reduce the size of plant required and could increase the profitably of treating the ore.

5. CONCLUSIONS

The flotation of these ores remains challenging. The suspected hand picked sampling methods used by the sample suppliers leads to non representative high grade values not ideal for flotation testing. The thorough analysis of the ore feed, concentrates and tails from a mineralogical standpoint will be essential to the further evaluation and understanding of the GS ore flotation response. These ores are complex in mineral content believed to be due to the history of formation with the initial sulphide deposit having undergone both sedimentary and metamorphic changes and atmospheric weathering. The response of copper oxide minerals was superior to the cobalt oxide minerals for all ore types tested. Future plans include the addition of specific cobalt collectors such as hydroxylates (J. Cuyper, 1999) and others after removal of the bulk of the micaceous material. However, some interesting results suggesting further investigation were obtained. These include the confirmation of two cobalt crystalline forms with different flotation responses.

Acknowledgement

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