Process Parameters for Bio-oxidation of Sulphur in the Pre-treatment of Bioleaching Residues Destined for Cyanide Gold Extraction

S. Mxinwa, R. Huberts, and M. Belaid

***Abstract*— A common problem faced during the recovery of valuable metals is the presence of impurities/unwanted elements. In order to retain a high concentration of a desired metal, all impurities which affect the metal's recovery should be removed before the final stage of recovery. In this work, research is conducted on the removal of residual sulphur from refractory gold bearing bioleach residue through the application of bio-oxidation, where sulphur is oxidized at different temperatures and pH levels to form sulphuric acid. Refractory sulphide ores and concentrates often consume large quantities of cyanide during leaching of gold using cyanide solution. Sulphides, elemental sulphur and many base metals react readily with cyanide, reducing the amount of cyanide available for leaching of the desired metal. So sulphur causes problems by increasing cyanide consumption and decreasing the environmental quality of the residue. In this research bacterial oxidation of sulphur was simulated in volumetric and Erlenmeyer flasks where inoculums were added to sulphur suspension to catalyse the oxidation of sulphur. Some of the flasks were operated at different pH levels and were controlled using a NaOH solution to investigate the optimum conditions of bacterial oxidation of sulphur. The controlled pH of 2.6 and a temperature of 50°C were found to be the best conditions for bacterial oxidation of sulphur. So this problem of sulphur consuming cyanide could possibly be overcome by controlling the pH at 2.6 and temperature at 50°C in the final stage of bacterial leaching gold plant using NaOH or some other neutralizing agent depending on the cost, which happens to enhance the kinetics of bacterial oxidation of sulphur. The operational conditions of moderate temperature and atmospheric pressure make this method very attractive from economic and environmental point of view.**

***Index Terms*—bacterial sulphur oxidation, bioleach residues, mesophiles, moderate thermophiles**

I. Introduction

SEVERAL methods have been proposed and applied for the oxidation of refractory gold sulphide ores including roasting, pressure oxidation, chemical leaching and bacterial oxidation. Gold ores are considered to be refractory if gold extraction from conventional cyanidation processes is less than 80% even after fine grinding. Such low extractions do not normally allow an economic recovery of the desired metal. Refractory gold concentrates must be treated before cyanidation [1].

Bacterial oxidation is a relatively new practice compared with roasting or pressure oxidation and is establishing itself as a feasible technique. Bacterial oxidation offers great advantages in contrast with other pyro or hydrometallurgical pre-treatments. The reagents cost is low and is carried out under atmospheric pressure and moderate temperature conditions, both of which reduce operational costs and environmental impact [1].

Bacterial oxidation is a process where a substance is oxidized using bacteria. It is very interesting from an environmental point of view; however the kinetics of this process are low [1]. Long residences times (several days, even weeks) cause excessive operational costs. In addition, sulphur may be left behind in the solid residue after bacterial oxidation, for example from the incomplete bio-oxidation of pyrrhotite as shown the following equation:

$$FeS + \frac{3}{4}O_2 + 3H^+ \rightarrow 3Fe^{3+} + S^0 + \frac{3}{2}H_2O \quad (1)$$

Refractory sulphide ores and concentrates frequently consume vast amounts of cyanide during leaching of gold using cyanide solution. Sulphides, elemental sulphur and many base metals react readily with cyanide, reducing the amount of cyanide available for leaching of the desired metal [4]. The solids containing sulphur are disposed to the environment according to Fig. 1 below. So sulphur causes problems by increasing the consumption of cyanide and also decreasing the environmental quality of the residues by forming thiocyanate which is very toxic to living organisms. Sulphur in the residue also reacts with water to form acid mine drainage [5]. This process is catalysed by bacteria. Ultimately the end product of bacterial sulphur oxidation is sulphate ion or sulphuric acid [3], as can be seen from the following net equations:

$$S^0 + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+ \quad (2)$$

$$S^0 + 3O_2 + 2H_2O \rightarrow 2HSO_4^- + 2H^+ \quad (3)$$

The application of removal of sulphur from gold bearing sulphide residue by bacterial oxidation prior to cyanidation is a promising choice for pre-treatment and it is believed to

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S. Mxinwa is with the Department of Chemical Engineering, University of Johannesburg, Doornfontein, Johannesburg 2028, South Africa, 2028 tel: +27730595312; email: sibabalwemxinwa@gmail.com
R. Huberts is with the Department of Chemical Engineering, University of Johannesburg, Doornfontein, Johannesburg 2028, South Africa, tel: +27115596517; email: roberth@uj.ac.za
M. Belaid is with the Department of Chemical Engineering, University of Johannesburg, Doornfontein, Johannesburg 2028, South Africa, tel: +27115596402; email: mbelaid@uj.ac.za

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decrease cyanide consumption and increase the recovery of gold [2].

In this research, bacterial oxidation was simulated in volumetric and Erlenmeyer flasks where inoculums and sodium hydroxide were added to suspensions to catalyse the oxidation of sulphur. It is envisaged that this process will take place after the main bacterial oxidation step that catalyses the breakdown of sulphides that host the gold.

This research work also investigates the possible ways of increasing the kinetics of this sulphur oxidation process thereby reducing the residence time, while keeping reagent costs low.

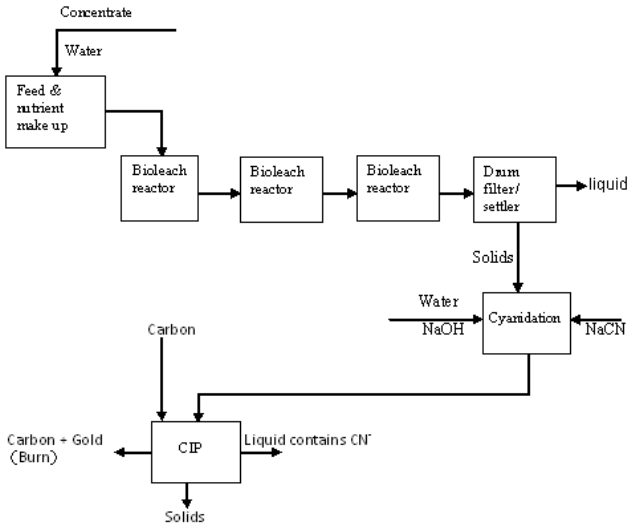

Fig. 1. Bacterial leaching gold plant

II. Experimental

A. Uncontrolled pH Levels

These bacterial sulphur oxidation experiments which had an uncontrolled pH were carried out in three 250ml Erlenmeyer flasks with 200ml of slurry. The first and the second Erlenmeyer flasks had slurries composed of 2 grams of elemental sulphur, 0.1 grams of 2:3:2 garden fertiliser, 10ml inoculums (mesophiles) and 190ml water, both of these flasks were operated at a temperature of 35^{o}C and were kept in a water bath. The third Erlenmeyer flask had slurry composed of 2 grams of elemental sulphur, 0.1 grams of fertiliser, 0.1 grams of yeast extract, 10ml inoculums (moderate thermophiles) and 190ml water and was operated at a temperature of 50^{o}C in a shaker incubator operating at 150 rpm. These temperature ranges were chosen because the mesophiles operate optimally at 35^{o}C and moderate thermophiles operate optimally at 50^{o}C [6].

B. Controlled pH

These bacterial sulphur oxidation experiments were carried out in seven 250ml volumetric flasks with 200ml of slurry, and their pH was controlled at different levels to identify optimum conditions of bacterial oxidation of sulphur. The pH levels were pH 1.5; 2.0; 2.6; 3.0 and 3.5. The pH level of 1.5 and 3.0 had duplicates to ensure the results found were correct. A solution of sodium hydroxide was used to control the pH. All these volumetric flasks had slurries composed of 2 grams of elemental sulphur, 0.1 grams of fertiliser, 10ml inoculums (moderate thermophiles) and 190ml water, and were operated at a temperature of 50^{o}C.

C. Equipment and Measurements

The equipment used to control the temperature at 35^{o}C was a water bath; it was deemed not advisable to use water bath for high temperatures (temperatures greater than 40^{o}C) because the water tends to evaporate at those temperatures. The incubator was used to control the temperature of 50^{o}C and shaking the flasks. The flasks were plugged with cotton wool to reduce the evaporation and prevent contamination but to allow a supply of air (oxygen). The pH profiles were measured almost daily with a Metrohm pH meter. A burette attached to a titration stand was used to ensure the correct amount of sodium hydroxide required to control the pH to the desired level was added. A balance was used to weigh the amount of elemental sulphur. Erlenmeyer and volumetric flasks were used to contain the elemental sulphur suspension. Funnels and filter papers were used to filter the amount of elemental sulphur retained at the end of the runs.

III. Results and Discussions

A. Uncontrolled pH Levels

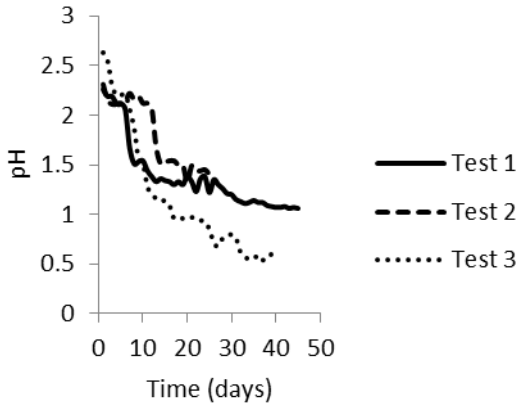

Fig. 2. Variation of pH with time

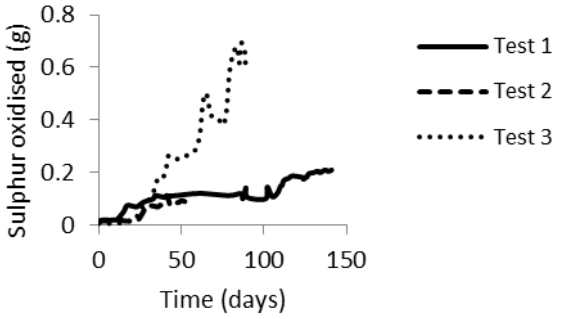

Fig. 3. Variation of sulphur oxidised with time

$$S^0 + H_2 0 + \frac{3}{2} O_2 \rightarrow H_2 SO_4 \quad (4)$$

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According to Fig. 2 and Fig. 3, all tests contained 2 grams of elemental sulphur initially and 200ml of water under aerobic, natural convection conditions. For test 1 the pH dropped from 2.26 to pH 1.06 and 0.2 grams of this elemental sulphur was consumed. pH 2.26 is equivalent to 0.036g S according to equation 2. A pH of 1.06 is equivalent to 0.574g of S, implying that 0.574g of sulphur (28.7%) was oxidized. This test operated at a temperature of 35^{o}C using mesophiles. For test 2 the pH dropped from pH 2.31 to pH 1.43 and 0.245 grams of this elemental sulphur (12.25%) was consumed after 52 days. This test operated at a temperature of 35^{o}C using mesophiles. For test 3 the pH dropped from pH 2.63 to pH 0.61 and 1.62 grams of this elemental sulphur was consumed after 90 days. This drop in pH value indicates that elemental sulphur was being oxidised under the influence of bacteria, and sulphuric acid was being produced from this oxidation, and Fig. 3 confirms this. From day 33 for test 1 and day 12 for test 2 the rate of pH drop was low. This may indicate that these bacteria were no longer active in catalysing the rate of oxidation at this stage; the reason might be that high sulphuric acid concentration was inhibiting the oxidation of sulphur due to le Chatelier's principle (see the equation for S^{o} oxidation, equation (2). The curve produced by these tests is not a smooth curve which means the rate at which the bacteria catalysed the rate of oxidation is not constant. Comparing test 1 and test 2 only 0.1 grams of test 2 was oxidised which means test 1 oxidised lot more elemental sulphur than test 2, this is because test 2 did not run for a long period as the test 1, after 52 days it had to be stopped because the pH was no longer dropping. Bacteria were assumed to be dead because the set point temperature was mistakenly increased from 35^{o}C to 50^{o}C and stayed there for days before the mistake was noticed. The temperature of 50^{o}C is too high for mesophilic bacteria. Looking at the pH curves, the pH in test 3 dropped at a faster rate compared to test 1and test 2, where mesophilic bacteria was used and a temperature of 35^{o}C with no shaker. Test 3 was operated at temperature of 50^{o}C and was a shaking flask which improves the mass transfer of oxygen from air to sulphur solution. This shows that the improved the mass transfer of oxygen and the presence of moderate thermophiles at a temperature of 50^{o}C accelerates the rate of oxidation. Test 1 and test 2 were supposed to show the similar behaviour because the amount of elemental sulphur, water and inoculums added was the same and also their operating conditions were the same until the temperature malfunction for the one flask.

TABLE I
SULPHUR OXIDISED

Tests	Number of Days	% oxidised
Test 1	141	38
Test 2	52	16
Test 3	90	81

According to table I, the percentages of elemental sulphur oxidised were calculated based on the weighed mass of elemental sulphur that remained. The amount of elemental sulphur of test 1 oxidised is 38% after 141 days of operation, the percentage of elemental sulphur oxidised in test 2 is 16% after 52 days of operation and the amount of elemental sulphur oxidised in test 3 is 81% after 90 days of operation. In this table it can also be seen that the rate of oxidation is faster in test 3 compared to the other tests. This confirms the above statement which says the improved mass transfer of oxygen and the presence of moderate thermophiles at the temperature of 50^{o}C accelerate the rate of oxidation. Hence thermophillic agitated conditions were chosen for further test work. The reason for the low sulphur breakdown results calculated from equation 2 could be explained by complexing of hydrogen ions with sulphate ions for example.

The percentages of sulphur oxidised in Fig. 3 are low compared to the one's in Table I, the percentages in Table I were calculated from the weighed amount of sulphur after oxidation and those in Fig. 3 are calculated using the stoichometry. This means that sulphur was not only converted to sulphuric acid but there were intermediate species formed.

B. Controlled pH

Further tests were done at different pH levels to identify the optimum conditions for bacterial oxidation of sulphur and their results are shown below. All these tests operated at the same temperature (50^{o}C), equal amount of sulphur, water, inoculums and rate of shaking (rpm) but their pH levels were different.

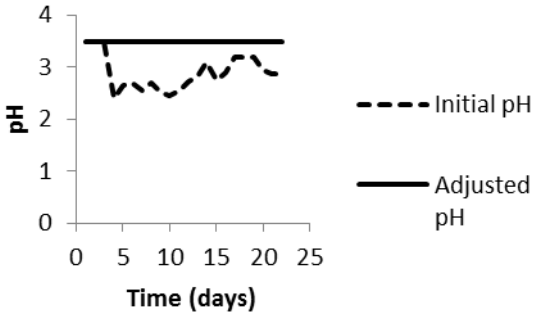

Fig. 4. Variation of pH for the pH 3.5 test

Fig. 4 shows that pH was dropping from a controlled pH of 3.5 to pH of around 2.5, indicating that sulphuric acid was being produced from the oxidation of elemental sulphur under the influence of moderate thermophiles. The solid line means the pH was being controlled to the pH of 3.5 and uneven dashed line shows the pH that was deviating from the controlled pH. The pH of this test started to drop after 5 days of operation, which means the bacteria took time to adapt at this pH. The gap or the area between the solid and the dashed trend is higher compared to other figures of pH of 2.6, 2.0 and 1.5, probably due to the fact that a small increase in hydrogen ion concentration will result in a large drop in pH at a higher pH level due to the logarithmic scale. It could also mean that more sulphur is being oxidized.

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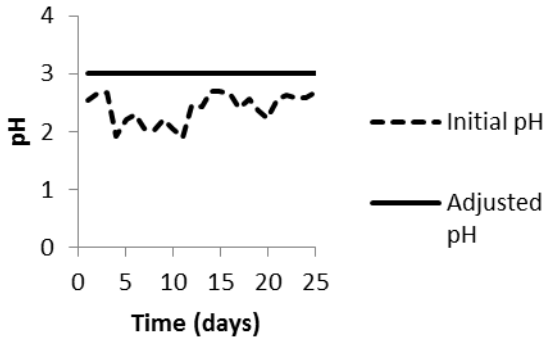

Fig. 5. Variation of pH for the pH 3.0 test

In Fig. 5, the graph shows that pH was dropping from a controlled pH of 3.0 to pH of around 2.2, this shows that sulphuric acid was being produced from the bacterial oxidation of elemental sulphur. The solid line means the pH was being controlled to the pH of 3.0 and uneven dashed line shows the pH that was deviating from the controlled pH. It did not take time for a pH to drop in this test, this means the bacteria adapt easily and fast at this pH. The gap or the area between the solid and the dashed trend is still higher compared to other figures of pH of 2.6, 2.0 and 1.5.

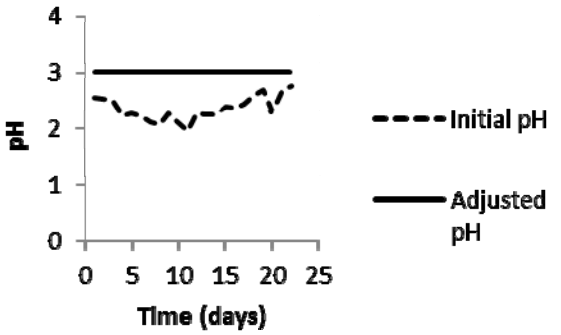

Fig. 6. Variation of pH for the pH 3.0 test(duplicate)

The test in Fig. 6 is a duplicate of the test above (Fig. 5) they show almost the same behaviour.

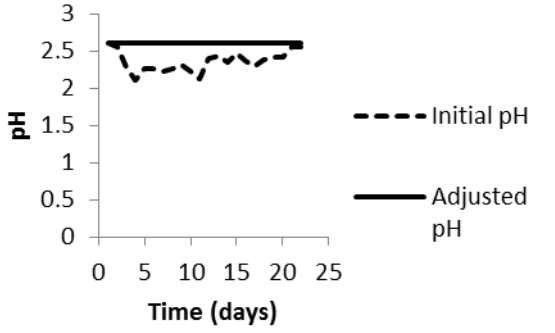

Fig. 7. Variation of pH for the pH 2.6 test

In Fig. 7, the graph shows that pH was dropping from a controlled pH of 2.6 to pH of around 2.2, this shows that sulphuric acid was being produced from the bacterial oxidation of elemental sulphur. The solid line means the pH was being controlled to the pH of 2.6 and dashed line shows the pH that was deviating from the controlled pH. It also did not take time for a pH to drop in this test; this means the bacteria adapt quick also at this pH. The gap or the area between the solid and the dashed line is smaller compared to that of pH of 3.5 and 3.0.

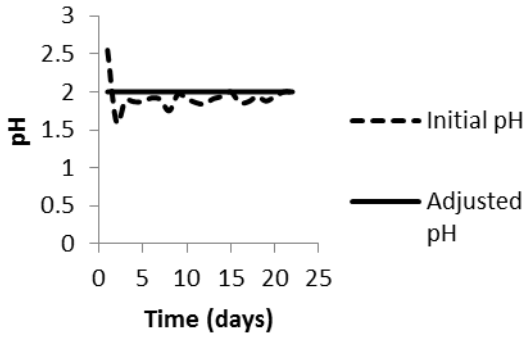

Fig. 8. Variation of pH for the pH 2.0 test

Fig. 8 shows that pH was dropping from a controlled pH of 2.0 to pH of around 1.9, although it did not drop much, indicating that sulphuric acid was being produced from the bacterial oxidation of elemental sulphur. The solid line means the pH was being controlled to the pH of 2.0 and uneven dashed line shows the pH that was deviating from the controlled pH. It also did not take a long time for a pH to drop in this test, meaning the bacteria adapted quickly to this pH. The gap or the area between the solid and the dashed line is smaller compared to that of pH of 3.5, 3.0, and 2.6.

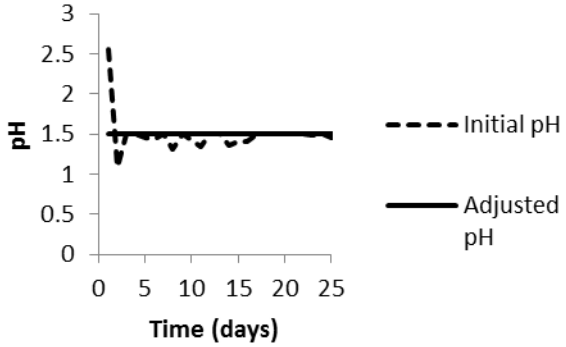

Fig. 9. Variation of pH for the pH 1.5 test

In fig 9, the graph shows that pH was dropping from a controlled pH of 1.5 to pH of around 1.47; this drop indicating that sulphuric acid was being produced from the bacterial oxidation of elemental sulphur even though the drop in pH was small. The solid line means the pH was being controlled to the pH of 1.5 and uneven dashed line shows the pH that was deviating from the controlled pH. Bacteria also adapted quickly to this pH, as the pH started

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dropping immediately. The gap or the area between the solid and the dashed line is very small compared to that of pH of 3.5, 3.0, 2.6 and 2.0. This could be due to the fact that a large increase in hydrogen ion concentration will only result in a small increase in pH level at the low pH levels. It could also mean that the oxidation rate of sulphur is slower compared to the ones at a pH of 3.5, 3.0, 2.6 and 2.0.

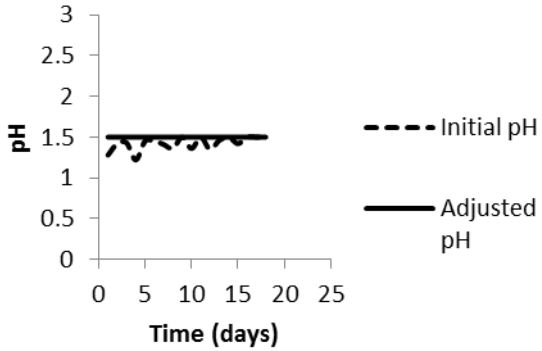

Fig. 10. Variation of pH for the pH 1.5 test (duplicate)

Fig. 10 is a duplicate of the above test (pH 1.5) and it behaved exactly the same way.

On the last days of the tests the dashed lines (pH) were not dropping much as compared to previous days in all the tests, which meant the bacteria were not very active at that stage. Perhaps the bacteria had run out of nutrients. It was deemed not advisable to add the nutrients again at this stage because it was almost the time of stopping the tests and unconsumed nutrients would increase the mass of the residue hence reducing the calculated sulphur oxidation percentage.

TABLE II
SULPHUR OXIDISED AFTER 45 DAYS

pHs	sulphur (g) oxidised after 45 days	% sulphur oxidised
pH 3.5	1.15	57.5
pH 3	1.585	79.25
pH 3 (duplicate)	1.607	80.35
pH 2.6	1.865	93.25
pH 2	1.462	73.1
pH 1.5	1.143	57.15
pH 1.5 (duplicate)	1.1368	56.84

TABLE III
SULPHUR OXIDISED AFTER 62 DAYS

pHs	sulphur (g) oxidised after 62 days	% sulphur oxidised
pH 3.5	1.68	84
pH 3.0	1.62	81
pH 1.5	1.34	67

In table II, the oxidation of sulphur based on the weight of remaining sulphur is given for the experiments that were run for 45 days. A pH level of 2.6 shows the highest percentage of elemental sulphur oxidised, with almost all of it being oxidised. The higher drop in pH level measured for the higher pH levels (Figs 4, Fig. 5 and Fig. 6) can therefore be explained by the logarithmic scale of pH, where the same increase in hydrogen ion concentration will cause a higher drop in pH at the higher pH levels. This needs to be confirmed by analysing sulphuric acid produced in the sulphur suspensions using an acid base titration.

Therefore the optimum condition of bacterial oxidation of sulphur is pH of 2.6, temperature of 50^{o}C and improved mass transfer of oxygen between air and liquid (agitation), with a small amount of reagents i.e. sodium hydroxide and nutrients. As the flasks were stopped and analysed for sulphur on day 45, the flasks at pH 3.5; 3.0 and 1.5 were allowed to continue running for next 17 days, so in total they ran for two months (62 days). Thereafter the percentage and mass of sulphur oxidised in controlled pH 3.5 was found to be 84% and 1.68 grams respectively as shown in Table III. For pH 3.0 the percentage and mass of sulphur oxidised was found to be 81% and 1.62 grams respectively and for pH 1.5 the percentage and mass of sulphur oxidised was found to be 67% and 1.34 grams respectively. Looking at the results obtained after 45 days as shown in Table II and those abstained after 62 days it can been that the sulphur oxidation at pH 3.5 after 62 days was higher than that for pH 3.0 after 45 days. This indicated that, given time, the bacteria will oxidize more sulphur at high pH levels.

IV. Conclusions

This study investigated the different conditions of bacterial oxidation of sulphur which included the comparing of bacterial oxidation kinetics at different pH levels. The results presented showed that a pH of 2.6 (controlled by NaOH addition) and temperature of 50^{o}C gives the faster rate of oxidation. The bacterial oxidation of sulphur by mesophiles is lower than that using moderate thermophiles and elevated mass transfer of oxygen. The literature reviewed showed that involving bacteria during pre-treatment of refractory gold bearing concentrates do not only catalyse the breakdown of sulphides that host the gold, but also the oxidation of the sulphur to sulphuric acid. Sulphur can be oxidised to a great extent due to the high breakdowns (greater that 90%). The operational conditions of moderate temperature and atmospheric pressure make this method very attractive from economic and environmental point of view.

V. Recommendations

Further test work is required using actual bacterial leach residues produced from refractory gold concentrates. As the pH levels in the test work dropped quickly, it is suggested to add the neutralizing agent more often, perhaps every 10

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hours, in order to improve the kinetics. Larger pilot scale work should follow using suitable reactors with an appropriate supply of oxygen and carbon (yeast extract) must be used to evaluate the economics of the process. The pH control must be implemented in an additional/the last stage of a bacterial leaching gold plant and not in the bioleach reactors because bioleach reactors might require a pH different from pH 2.6 for the oxidation of sulphide minerals. The economics of implementing the additional stage need to be assessed – the cost of additional process vs cost saving due to lower cyanide consumption and less environmental pollution.

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REFERENCES

[1] N. Iglesias and F. Carranza, “Treatment of a gold bearing arsenopyrite concentrate by ferric sulphate leaching” Department of chemical engineering. University of Sevilla, Spain
[2] N. Iglesias and F. Carranza, “Bacterial leaching of copper ore rich in gold and silver” Department of chemical engineering. University of Sevilla, Spain
[3] G. S. Simate, S. Ndlovu, and M. Gericke, “The effect of elemental sulphur and pyrite on the leaching of nickel literates using chemolithotrophic bacteria” Hydrometallurgy conference, 2009. The Southern African institute of mining and metallurgy.
[4] J. Vandy, S. Shranda and X. Sharon “Factors affecting the elemental sulphur formation in biooxidised samples” Harward, Califonia
[5] S. C. Campbell, G. J. Olson, T. R. Clark and G. McFeters, “Biogenic production of cyanide and its application to gold recovery” Center of biofilm engineering and microbiology department. Montana State University. Bozeman.
[6] D. W. Dew, C. Van Buuren and K. McEwan “Bioleaching of base metal sulphide concentrates: A comparison of mesophile and thermophile bacterial cultures” Billiton process research, Randburg, South Africa.

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