

*Received April 15, 2012; reviewed; accepted June 15, 2012*

## **PRESSURE OXIDATION OF PYRITE-ARSENOPYRITE REFRACTORY GOLD CONCENTRATE**

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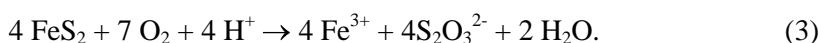
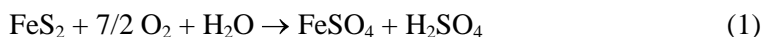
**Abstract:** Refractory gold ores have poor gold recoveries with direct cyanide leaching. Typically the refractoriness is due to encapsulation of the gold particles inside the host mineral. To liberate gold for leaching the host mineral must be broken by mechanical or chemical means. The aim of this study was to study the effect of temperature, oxygen partial pressure and slurry density on pressure oxidation of pyrite-arsenopyrite gold concentrate. Batch oxidation tests in an autoclave were done using a factorial design. Different responses were measured and analysed to study effect of the three factors and oxidation kinetics. Generally, high slurry density required high temperature and oxygen partial pressure to reach complete oxidation. Oxidation kinetics at 225°C temperature, with 1050 kPa oxygen partial pressure and 15% slurry density was found to be fastest resulting in complete conversion of sulfides in 30 minutes. At 195°C, 700 kPa oxygen partial pressure and 10% slurry density, the oxidation kinetics for complete sulfide conversion was about 60 minutes. Slurry densities above 10% had an adverse effect on the oxidation rate, when the temperature was below 225°C and oxygen partial pressure below 1050 kPa.

**Keywords:** *gold ore, hydrometallurgy, leaching, factorial design*

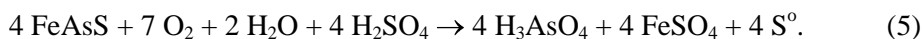
### **Introduction**

Many of the gold deposits today contain gold finely disseminated in iron sulfide minerals, such as pyrite and arsenopyrite. Such deposits are known as refractory gold ores due to encapsulation of fine gold particles in the host mineral (Iglesias and Carranza 1994; Fleming 1992; Corrans and Angove 1991). A clear border between refractory and non refractory ore in terms of gold recovery is not given, but several authors have stated that less than 80% gold recovery by direct cyanide leaching after fine grinding of the ore indicates a refractory ore (Iglesias and Carranza 1994; Fleming 1992; Corrans and Angove 1991; Pangum and Browner 1996). The refractory ore must be broken down by chemical means, with utilization of oxidative processes, such as roasting, pressure oxidation or bacterial leaching. These expose the valuable metals to subsequent cyanidation.

Leaching of metal sulfide minerals is commonly considered as an electrochemical reaction between sulfide ion and oxygen. Sulfide sulfur is oxidized either into elemental sulfur, sulfite or sulfate ions. Oxygen undergoes a reduction reaction with water formation (Bailey and Peters 1976; Rimstidt and Vaughan 2003; Papangelakis and Demopoulos 1990; Long and Dixon 2004). All these studies present two competing reactions to occur as the anodic oxidation reaction of pyrite, one producing sulfate and sulfuric acid (1) and the other sulfate and elemental sulfur (2). Oxygen can also oxidize pyrite directly producing  $\text{Fe}^{3+}$  and thiosulfate (3) followed by thiosulfate decomposition and oxidation of the resulting sulfite ion to sulfate (Long and Dixon 2004).



The proposed reactions of arsenopyrite are quite identical (Eqs (4) and (5)) (Papangelakis and Demopoulos 1990)



Pressure oxidation is typically operated in temperatures of 190 to 230°C and oxygen overpressure of 350 to 700 kPa (Fleming 2010). Under these conditions sulfide sulfur is oxidized into sulfates and bisulfates and iron dissolves as ferrous iron or ferric iron. Ferric iron can hydrolyse and precipitate as hematite, basic iron sulfate or jarosite, and also formation of elemental sulfur as oxidation product is possible. High temperatures are required to avoid formation of elemental sulfur, which is detrimental for cyanidation due to excess consumption of cyanide. In this work the effect of temperature, oxygen partial pressure and slurry density on oxidation kinetics and conversion were studied using batch tests in an autoclave.

## Experimental

Refractory gold concentrate was supplied from pyrite-arsenopyrite mineralization in northern Finland. Minerals recognized from the concentrate with XRD were pyrite 24.7%, arsenopyrite 27.1%, quartz 10.7%, and less than 10% each of albite, dolomite, microcline, anorthite and chlorite. Coulter Counter analysis showed that majority of the particles were 1 to 300  $\mu\text{m}$ . Chemical analysis of the concentrate in wt-% was As 6.0%, Fe 21.6%, C 3.3%, S 19.5%, elemental S 0.25%, sulphate 0.42%, and Cl 0.007%. For the pressure oxidation experiments 99.5% pure oxygen was used. A 20  $\text{g}/\text{dm}^3$  sulfuric acid solution was prepared from laboratory grade 95–97% sulfuric acid and distilled water.

Autoclave oxidation tests were conducted in Büchi ecoclave model 075 titanium autoclave. The total volume of the autoclave vessel was about 1.1 dm<sup>3</sup> and it was equipped with magnetic agitation unit, gas inlet and outlet, and sampling system with nitrogen flush that was also used for nitrogen feed into the vessel. The jacket of the reactor had inbuilt electric heating and cooling water circulation for temperature control. Pitched blade propeller and agitation speed 650 rpm were used in all experiments. Oxygen pressure was adjusted with pressure drop valve and oxygen flow was measured with oxygen mass flow meter.

Dried and homogenized sample was used in all of the experiments. For each test a sample of concentrate and 750 cm<sup>3</sup> sulfuric acid were loaded into the reactor. Nitrogen was purged to remove oxygen. Reactor was then heated with the heating resistors in the reactor jacket. Each test was started when oxygen feed was started. Oxygen feed pressure was adjusted before the experiment start as a sum of the water vapour pressure at experiment temperature and the desired oxygen overpressure. Every experiment was run for sixty minutes and the end of experiment was closing the oxygen inlet valve. Immediate cooling of the reactor was started. Slurry drain was done at temperature of about 80°C. Slurry was left for decantation, and in two hours from the draining pH and redox potential of the solution versus a calomel electrode were measured. Dried solids were analysed for total sulfur content, elemental sulfur and sulfate sulfur. Filtered solutions were analysed for dissolved iron. Total amount of consumed oxygen was integrated using the measured oxygen mass flow. Conversion of iron was calculated by dividing the amount of dissolved iron by the amount of iron charge. Conversion of sulfide was calculated as difference between residual sulfide amounts and initial sulfide amount in relation to the initial sulfide amount.

Table 1. Factorial design of experiments

Test Std number	Temperature, °C	Oxygen partial pressure, kPa	Slurry density, %
1	165	350	15
2	225	350	5
3	165	1050	5
4	225	1050	15
5	165	350	15
6	225	350	5
7	165	1050	5
8	225	1050	15
9	195	700	10

This study was planned as half factorial to ensure the reliability of the main factor analysis. Experimental setup was four different combinations of selected three factors with two replicates (Table 1). The centre point was replicated three times. Replication gives more reliability on the analysis of the main factors, but a half factorial setup lacks on the analysis of the interactions of the factors. Factorial analysis of the varia-

bles was made with MINITAB 16 statistic calculation software. Three major analyses were conducted. Pareto analysis shows the significance of the factor to the measured response. Main factor analysis shows the effect of each individual factor on the measured response. Interaction plot shows how two factors affect the response together.

## Results

The oxidation of concentrate was followed during the test by measuring oxygen consumption. The experiment had a set value for oxygen partial pressure and that pressure was maintained by controlling oxygen feed. The oxygen was consumed in the oxidation reactions and therefore oxygen flow is a measure of reactions proceeding. The effect of temperature, oxygen pressure and slurry density were measured using a factorial experimental design. The effect of these factors was estimated from the solution redox potential and iron concentration and solids sulfur concentration after completing the experiment.

## Oxidation kinetics

Oxygen consumption was measured online during the oxidation test. It was assumed that the oxidation is complete when oxygen feed is no longer needed to maintain reactor pressure. This is reasonable if the reaction proceeds with direct oxidation of the sulfides as suggested for pyrite in Eq. (3) (Long and Dixon 2004). Figure 1 shows four different types of oxygen consumption curves noticed in the tests. When using

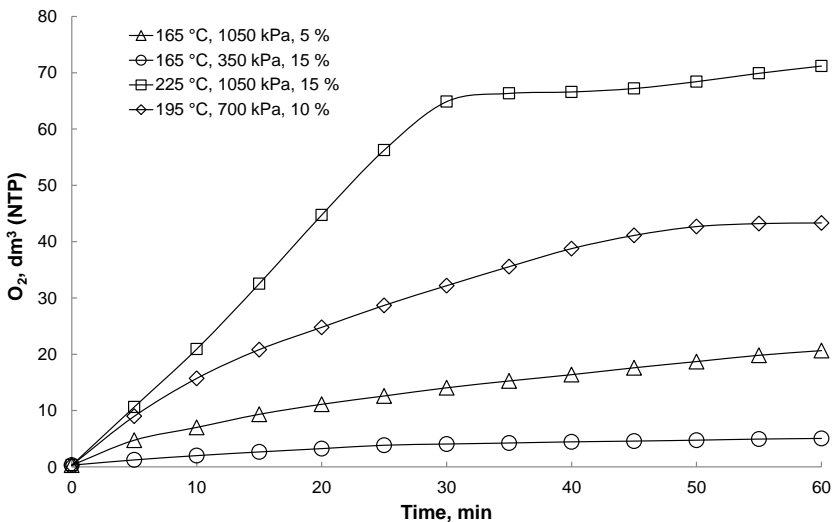


Figure 1. Examples of calculated oxygen consumptions

low temperature and low oxygen pressure the oxygen consumption was small and either reached a very low steady level soon after the beginning (test 5, 165°C,

350 kPa, 15%) or increased very slowly (test 3, 165°C, 1050 kPa, 5%). At higher temperature and oxygen pressure the oxygen consumption was more rapid and reached a steady level in 55–60 minutes (test 9 I, 195°C, 700 kPa, 10%). At highest temperature and oxygen pressure the oxygen consumption was even more rapid and reached a high steady level in 30 minutes (test 8, 225°C, 1050 kPa, 15%).

The oxygen consumption rates at the beginning of the test were estimated from curves like shown in Figure 1. They varied from 0.14 dm<sup>3</sup>/min in test 5 (165°C, 350 kPa, 15%) to 2.2 dm<sup>3</sup>/min in test 8 (225°C, 1050 kPa, 15%). Some of the experiments showed clear changes in cumulative oxygen consumption and these were taken as points where sulfide conversion had reached its maximum value. This was taken as the endpoint of the oxidation. Table 2 shows the initial oxygen consumption rates, endpoints and the cumulative oxygen consumption to the endpoint. Note that test number four is missing due to equipment malfunction.

Table 2. The initial oxygen consumption rates, endpoints and the cumulative oxygen consumption to the endpoint determined from online oxygen flow measurements

Test	Initial O <sub>2</sub> , dm <sup>3</sup> /min	Endpoint, min	Cumulative O <sub>2</sub> , dm <sup>3</sup>
Std1 (165°C, 350 kPa, 15%)	0.19	No endpoint	Not estimated
Std2 (225°C, 350 kPa, 5%)	0.84	60	47.6
Std3 (165°C, 1050 kPa, 5%)	0.52	No endpoint	Not estimated
Std4 (225°C, 1050 kPa, 15%)	–	–	–
Std5 (165°C, 350 kPa, 15%)	0.14	25	3.85
Std6 (225°C, 350 kPa, 5%)	0.35	30	11.9
Std7 (165°C, 1050 kPa, 5%)	0.59	No endpoint	Not estimated
Std8 (225°C, 1050 kPa, 15%)	2.20	30	64.9
Std9 (195°C, 700 kPa, 10%)	0.95	No endpoint	Not estimated
Std9 I (195°C, 700 kPa, 10%)	1.0	55	42.0
Std9 II (195°C, 700 kPa, 10%)	0.93	60	43.1

The results in Table 2 indicate that oxygen consumption at the beginning of oxidation increases with increasing temperature, oxygen pressure and slurry density. A bigger charge requires more oxygen and it is delivered sufficiently only in experiments with high temperature and oxygen pressure. The appearance of an endpoint indicates that no further oxidation happens but it does not necessarily mean that the sulfide conversion is complete.

### The effect of oxidation factors

The conversion of sulfides after the test was estimated using redox potential of the solution, iron concentration of the solution and remaining sulfur in the residue. The effect of temperature, oxygen pressure and slurry density were analysed using factorial setup. Measurements and values of the calculated responses are presented in Table 3.

The oxygen columns refer to oxygen consumed in the first 20 minutes and during the whole 60 minutes. Due to agitation problems at high temperatures test number 4 failed and for conducting the factorial analysis its results were copied from the replicate test number 8. For the same reason during test 6 the agitation stopped after about 30 minutes from the start of the experiment and did not return until the end of the experiment. The reason was later identified as thermal expansion of the bearings that resulted in seizing.

Table 3. Measured pH, redox and oxygen consumption values and calculated iron and sulfide conversion

Test	pH <sub>init.</sub>	pH <sub>fin.</sub>	E <sub>redox</sub> , mV SCE	O <sub>2</sub> /20, dm <sup>3</sup>	O <sub>2</sub> /60, dm <sup>3</sup>	Fe <sub>conv</sub> , %	S <sub>conv</sub> , %
Std1 (165°C, 350 kPa, 15%)	0.67	7.38	247	4.7	10.9	0.003	-3.4
Std2 (225°C, 350 kPa, 5%)	0.70	0.51	562	19.4	47.6	29.6	100.0
Std3 (165°C, 1050 kPa, 5%)	0.86	0.81	497	11.1	20.7	62.6	83.0
Std4 (225°C, 1050 kPa, 15%)	--	--	--	--	--	--	--
Std5 (165°C, 350 kPa, 15%)	0.76	7.14	237	3.2	5.1	0.005	-1.7
Std6 (225°C, 350 kPa, 5%)	0.59	0.93	442	9.9	15.5	18.3	9.1
Std7 (165°C, 1050 kPa, 5%)	0.74	0.52	501	12.8	20.1	59.9	85.3
Std8 (225°C, 1050 kPa, 15%)	0.88	0.47	621	44.6	71.2	40.8	99.6
Std9 average (195°C, 700 kPa, 10%)	0.60	0.24	580	23.5	43.3	41.0	100.0

Calculated constant and coefficients for regression equations for each response are presented in Table 4. The R<sup>2</sup> values show that three responses, oxygen consumption after 20 minutes, discharge solution redox potential and iron conversion at the end of the experiment, have good fitting of the regression model with over 90% goodness of fit. Two other responses, total oxygen consumption and conversion are less well modelled by the regression equation.

Table 4. Regression equation constant and coefficients  $\alpha$  for each response

Response	Constant	$\alpha(T)$ , °C	$\alpha(pO_2)$ , kPa	$\alpha(\text{slurry density})$ , %	R <sup>2</sup>
O <sub>2</sub> 20 min, dm <sup>3</sup>	-81.6	0.36	0.03	1.10	0.92
O <sub>2</sub> 60 min, dm <sup>3</sup>	-128	0.62	0.04	1.36	0.81
E <sub>redox</sub> , mV SCE	-274	3.18	0.27	-6.87	0.93
Fe <sub>conv</sub> , %	31.5	0.87	19.5	-11.1	0.97
S <sup>2-</sup> <sub>conv</sub> , %	-76.3	0.46	0.09	-2.46	0.66

In Table 4 the trends in oxygen response are the same as were found for initial oxygen consumption rate. An increase in the redox potential and higher conversions indicate that more of the sulfide has been oxidized. For these responses the increases in temperature and oxygen pressure are beneficial whereas increase in slurry density

decreases the response value. According to the Tromans model (Tromans 1998) oxygen solubility increases both with increasing temperature and oxygen pressure and so the dissolution reactions (1)–(5) will proceed further. When the temperature and oxygen pressure are too low and slurry density is too high there is not enough dissolved oxygen to oxidize sulphide completely.

## Discussion

Analysis of Tables 3 and 4 show that discharge solution redox potential is clearly correlated with consumed oxygen (Fig. 2). Assuming that the sulfide oxidation proceeds with direct oxidation by dissolved oxygen and produces ferric ions (Long and Dixon 2004) the more oxygen is consumed the higher is the amount of ferric iron. According to Nernst equation increasing ferric iron concentration increases the redox potential logarithmically. In the experiments done at 195°C and 225°C redox potential was higher and at 165°C lower than the standard electrode potential of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  equilibrium. At the lowest temperature there is not enough oxidizing power to convert iron to ferric iron or the ferric iron produced has been reduced to ferrous iron in oxidation of concentrate. Sulfur compounds in the solution can also reduce ferric iron. For example decomposition of thiosulfate produces elemental sulfur and sulfite, which is oxidized by ferric iron to sulfate (Long and Dixon 2004).

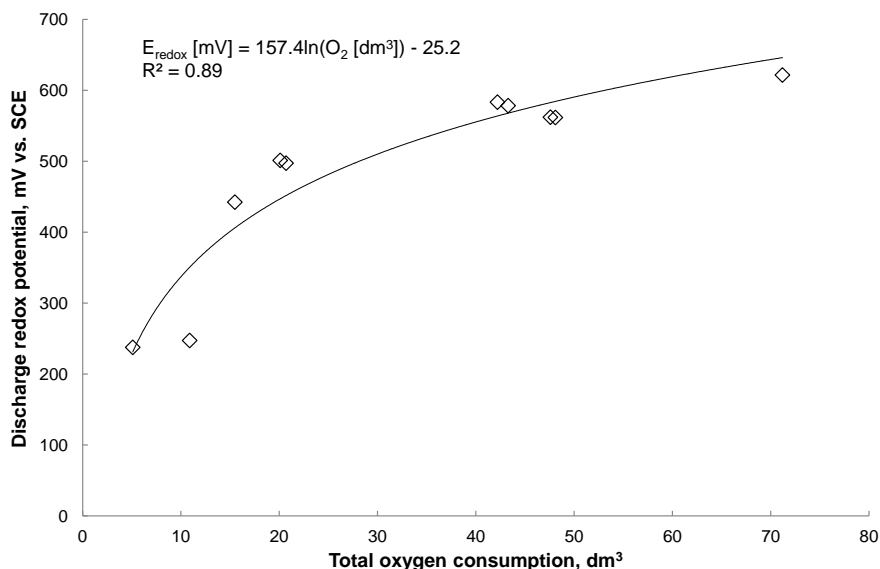


Figure 2. Discharge solution redox potential after the experiment as a function of oxygen consumed during the oxidation test

The iron and sulfide conversions describe how much of the concentrate charge iron has dissolved in the solution and how much of the sulfide sulfur remained in the leaching residue. The iron and sulfide conversions as function of oxygen consumed during the test are shown in Fig. 3. The conversion of sulfide is quite well described with a logarithmic equation. Using a high temperature and oxygen pressure the conditions are suitable for oxidation and complete conversion can be achieved. The iron conversion is less well described with a logarithmic equation. As shown by equations (1)–(5) iron should produce soluble sulfates. The low conversion values indicate that iron has been precipitated back. Especially the tests with high oxygen consumption suggest that iron has been oxidized to ferric iron, hydrolysed and converted to solid iron compounds.

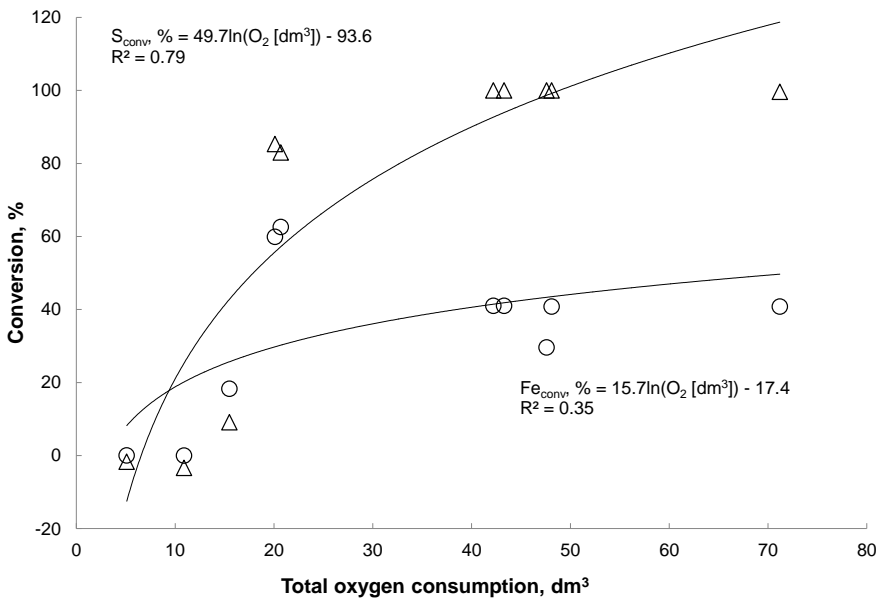


Figure 3. Iron and sulfur conversions after the experiment as a function of oxygen consumed during the oxidation test

## Conclusions

Oxidation of the pyrite-arsenopyrite concentrate is improved by higher temperature and oxygen pressure and these are linked to the amount of dissolved oxygen. If these factors are high enough and charge size small enough, oxidation is completed in 30–60 minutes. The higher are temperature and oxygen pressure the more rapid is oxidation.

Factorial testing indicates that all three studied factors affect conversion of the concentrate minerals. Oxygen pressure is the most important. It is possible that the effect



of temperature is not shown clearly as it is linked to the concentration of dissolved oxygen.

The conversion of the concentrate minerals was estimated using discharge redox potential describing  $\text{Fe}^{3+}/\text{Fe}^{2+}$  equilibrium, iron conversion using discharge iron concentration and sulfur conversion using leaching residue sulfide concentration. Of these responses the sulfide conversion is most useful as ferric iron can react to insoluble compounds.

### Acknowledgements

This work has been done in the LOWGRADE project of the ELEMET research program funded by FIMECC Oy. The financial support of TEKES and Outotec Oyj is gratefully acknowledged.

### References

- IGLESIAS, N., CARRANZA, F., 1994, *Refractory gold-bearing ores: a review of treatment methods and recent advances in biotechnological techniques*. *Hydrometallurgy* 34, 3, 383–395.
- FLEMING, C.A., 1992, *Hydrometallurgy of precious metals recovery*. *Hydrometallurgy* 30, 1–3, 127–162.
- CORRANS, I.J., ANGOVE, J.E., 1991, *Ultra fine milling for the recovery of refractory gold*. *Minerals Engineering* 4, 7–11, 763–776.
- PANGUM, L.S., BROWNER, R.E., 1996, *Pressure chloride leaching of a refractory gold ore*. *Minerals Engineering* 9, 5, 547–556.
- BAILEY, L.K., PETERS, E., 1976, *Decomposition of pyrite in acids by pressure leaching and anodization: the case for an electrochemical mechanism*. *Canadian Metallurgical Quarterly* 15, 4, 333–344.
- RIMSTIDT, J.D., VAUGHAN, D.J., 2003, *Pyrite oxidation: a state-of-the-art assessment of the reaction mechanism*. *Geochimica et Cosmochimica Acta* 67, 5, 873–880.
- PAPANGELAKIS, V.G., DEMOPOULOS, G.P., 1990, *Acid Pressure Oxidation of Arsenopyrite: Part I, Reaction Chemistry*. *Canadian Metallurgical Quarterly* 29, 1, 1–12.
- LONG, H., DIXON, D.G., 2004, *Pressure oxidation of pyrite in sulfuric acid media: a kinetic study*. *Hydrometallurgy* 73, 3–4, pp. 335–349.
- FLEMING, C.A., 2010, *Basic iron sulfate – a potential killer in the processing of refractory gold concentrates by pressure oxidation*. *Minerals & Metallurgical Processing* 27, 2, 81–88.
- TROMANS, D., 1998, *Oxygen solubility modeling in inorganic solutions: concentration, temperature and pressure effects*. *Hydrometallurgy* 50, 3, 279–296.