JOURNAL OF APPLIED ELECTROCHEMISTRY **25** (1995) 852–856

A voltammetric investigation of the oxidation of pyrite in nitric acid solutions: relation to treatment of refractory gold ores

J. R. FLATT

Garrell School of Mining, Metallurgy and Applied Geology, University of South Australia, The Levels, S.A. 5095, Australia

R. WOODS

CSIRO Division of Minerals, PO Box 124, Port Melbourne, Victoria 3207, Australia

Received 23 August 1994; revised 23 January 1995

The anodic oxidation of pyrite on potential scans has been investigated in 0.22 mol dm^{-3} nitric acid over the temperature range 26 to 80 °C. The relative formation of sulphur and sulphate was determined from the anodic and cathodic charges associated with different regions of the voltammogram. It was found that the percentage of pyrite oxidizing to sulphur decreased with increase in potential to reach a negligible value at ~1.5 V vs SHE. No discernible change was observed in the potential dependence of the relative formation of sulphur and sulphate when the reaction temperature was varied. The significance of these results on the nitric acid treatment of refractory (sulphidic) gold ores is discussed.

1. Introduction

In many refractory gold ores, the precious metal is contained within sulphide minerals, in particular pyrite and arsenopyrite. To achieve acceptable recovery of gold from such ores, it is necessary first to oxidize the sulphides. Such pretreatment renders the gold accessible to leaching by conventional cyanidation procedures. A number of approaches to release the gold from sulphidic ores are being promoted [1], namely, roasting, pressure oxidation, biological oxidation and oxidation with nitric acid. The latter is the basis of the Redox (Arseno) [2], the Nitrox [3] and the HMC 'Hydromet' processes [4].

The chemistry of the high and low temperature versions of the Redox process and of the Nitrox process is essentially the same. Oxidation of the sulphide mineral with nitric acid produces gaseous nitric oxide which is subsequently converted back to nitric acid by reaction with oxygen either *in situ* or in an external regeneration system. Thus, the process can be considered as the reaction of sulphide minerals with oxygen, catalysed by nitric acid. The use of nitric acid as an intermediary involves a slight loss in thermodynamic oxidizing power; the standard reduction potential for nitric acid (Reaction 1 below) is 0.96 V vs SHE compared with 1.23 V for oxygen. However, its use has the kinetic advantage that mass transfer of the oxidant to the mineral surface is very efficient and not limited by the rate of oxygen transfer from the gas phase to the liquor, or by the oxygen solubility in the aqueous system at elevated temperatures.

Sulphide minerals can oxidize to elemental sulphur or directly to sulphate, depending on the identity of the mineral and the reaction conditions. The formation of sulphur leads to complications in the treatment of refractory gold ores by the Redox and Nitrox processes for a number of reasons. Agglomeration by elemental sulphur can inhibit sulphide oxidation. The presence of elemental sulphur in the product of preoxidation can inhibit gold cyanidation and lead to high cyanide consumption through reaction to form thiocyanate. To minimize these complications, either elemental sulphur formation needs to be avoided or any sulphur formed needs to be further oxidized to sulphate.

Pilot plant studies [5] have applied high temperatures (195 °C) and pressures (2000 kPa) to oxidize elemental sulphur during the preoxidation stage. One of the challenges in developing nitric acid process routes is to identify less severe conditions under which the quantity of sulphur in the reaction product is insignificant. The detailed chemistry of elemental sulphur formation during nitric preoxidation has not been reported in the literature. The present electrochemical work constitutes part of an extensive study to elucidate this chemistry.

The major product of the decomposition of nitric acid in the nitric acid oxidation of sulphide minerals is generally considered [1] to be nitric oxide. The overall process is expected to proceed via an anodic oxidation of the sulphide coupled with the cathodic

0021-891X

reduction of nitric acid:

$$HNO_3 + 3H^+ + 3e^- \longrightarrow NO + 2H_2O \quad (1)$$

The anodic oxidation of pyrite can follow two alternative routes. These are

$$FeS_2 \longrightarrow Fe^{3+} + 2S^0 + 3e^- \quad (2)$$

and

$$FeS_2 + 8H_2O \longrightarrow Fe^{3+} + 2SO_4^{2-} + 16H^+ + 15e^- \quad (3)$$

Thus, the conditions for an effective pretreatment method for pyritic gold ores must result in Reaction 3 being the dominant oxidation process.

The relative rates of Reactions 2 and 3 have been determined by a number of authors covering a range of potentials (or current densities), temperatures and supporting electrolytes. Bailey and Peters [6] studied the oxidation of pyrite in 1 mol dm^{-3} $HClO_4$ at 110 °C and found that 60–90% of the mineral followed the sulphate pathway with the higher values corresponding to higher potentials. Nagai and Kiuchi [7] also oxidized pyrite at elevated temperatures (up to 175 °C) using 0.5 mol dm^{-3} H_2SO_4; these authors found the ratio of sulphate to sulphur to vary with temperature and current density and to lie in the range 1 : 4 to 1 : 1.

Biegler and Swift [18] carried out a mechanistic study of the anodic behaviour of pyrite in acid solutions at 25 °C. They concluded that the formation of sulphur and sulphate follow independent pathways; i.e., Reaction 2 is not the first step in Reaction 3. The stoichiometry of the anodic reaction was determined as a function of potential and the sulphate yield was found to approach 100% at ~1.5 V vs SHE. These authors also found that the potential dependence of their sulphate:sulphur ratios was similar to that reported by Bailey and Peters [6] for oxidation at 110 °C and suggested that the sulphate yield at fixed potential may be independent of temperature.

Lowson [9] also plotted the stoichiometry of the anodic oxidation of pyrite reported by Biegler and Swift [8] and Bailey and Peters [6] as a function of potential, but included data reported for 145 °C by Nagai and Kiuchi [7] and for 25 °C by Meyer [10]. Although this comparison did not negate the conclusion reached by Biegler and Swift regarding the absence of a temperature dependence, the scatter generated by the results of the additional authors introduced a larger degree of uncertainty to this conclusion.

The above studies of the anodic oxidation of pyrite involved solution analysis to determine reaction stoichiometry. In a study in solutions of pH 4.6, 9.2 and 13, Hamilton and Woods [11] derived the ratio of the sulphate to sulphur formed from the charges passed in different features of voltammograms. The present communication presents the results of a voltammetric study of pyrite oxidation in acid solutions over a range of temperatures with a view to determining conditions under which sulphur formation is eliminated or minimised. Nitric acid was selected as the supporting electrolyte to relate the results to nitric acid processing, but the concentration was restricted to 0.22 mol dm^{-3} so that sulphur reduction could be resolved from reduction of nitric acid (Reaction 1). A comparison of the electrochemical findings with those of leaching studies will be presented in a future publication.

2. Experimental details

Electrodes were prepared from massive crystals of pyrite from Gumeracha, South Australia. A specimen cut from the pyrite sample was attached onto a threaded brass fitting using silver epoxy and encased in epoxy resin as described previously [12]. Before each voltammetric experiment, a fresh pyrite surface was created by abrading the electrode on 200 grade silicon carbide paper under a stream of distilled water deoxygenated with nitrogen. Earlier work [13] established this method to be satisfactory in minimizing surface oxidation of the mineral provided the electrode was rapidly transferred to the electrochemical cell.

Potentials were controlled with a Pine Instruments Model AFRDE4 potentiostat with in-built sweep generator and current-potential relationships were plotted on a Rikadenki X–Y recorder. All scans were carried out at 20 mV s^{-1}. Potentials were measured against a saturated calomel electrode (SCE) contained in a side compartment and connected to the main cell via a Luggin probe. The potentials were converted to the standard hydrogen electrode (SHE) scale taking the potential of the SCE to be 0.244 V against the SHE [14].

Freshly ground electrodes were transferred to the electrochemical cell which was held within 1 °C of the target temperature in a water bath. Several seconds were allowed for the electrode temperature to equilibrate with the electrolyte and a positive-going scan applied from a potential close to the rest value. The scan was reversed at selected upper potential limits and a negative-going scan applied to a lower limit selected to ensure complete reduction of any sulphur produced by anodic oxidation of the pyrite. The scan was again reversed and a positive-going scan recorded to the rest potential. Both the X and Y scales were altered during the potential cycle when required to allow accurate integration of the charges passed on the voltammogram.

3. Results and discussion

Figure 1 presents voltammograms from a pyrite electrode on 0.5 mol dm^{-3} sulphuric acid and 0.22 mol dm^{-3} nitric acid solutions at 25 °C. It can be seen that anodic oxidation on the positive-going scans commenced at a similar potential in the two electrolytes. Also, that a higher current was observed in the nitric acid medium. The anodic currents are due

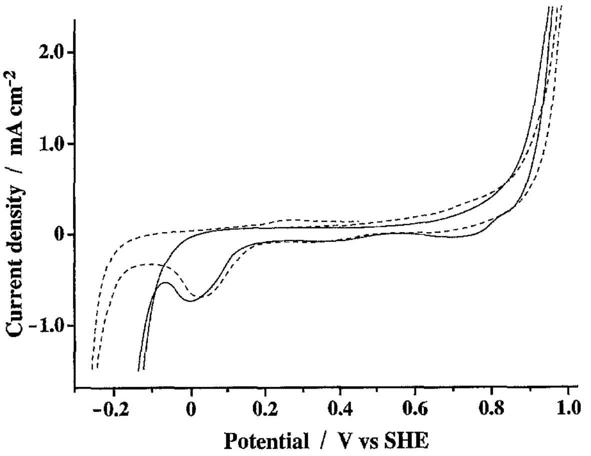

Fig. 1. Cyclic voltammograms for a pyrite electrode at 25 °C in (——) 0.22 mol dm^{-3} nitric acid and (·····) 0.5 mol dm^{-3} sulphuric acid. Scans at 20 mV s^{-1} commenced at 0.2 V and taken initially in the positive-going direction.

to a combination of Reactions 2 and 3. On the return scan, a cathodic peak appears at ~0 V on each curve due to reduction of sulphur formed by Reaction 2 according to the following reaction:

$$S + 2H^+ + 2e^- \longrightarrow H_2S \qquad (4)$$

As the scan is taken to more negative values, the cathodic current increases to large values with the increase commencing at ~0.1 V less-negative potentials with nitric than with sulphuric acid. This difference is considered to arise from the different processes that limit the accessible potential range. With sulphuric acid, the major cathodic reactions at pyrite were shown [15] to be reduction of the mineral to release H_2S together with hydrogen evolution derived from reduction of the acid electrolyte. The limiting process with nitric acid will be the reduction of the electrolyte by Reaction 1. It can be seen from Fig. 1 that the charge arising from Reaction 4 can be separated from that due to Reaction 1, and hence that sulphur formation can be determined in the nitric acid solution at the concentration selected.

Figure 2 shows positive-going voltammograms for a pyrite electrode in 0.22 mol dm^{-3} nitric acid at 26, 40, 60 and 80 °C. It can be seen that an anodic current flows at potentials >0.8 V, increasing steeply with increase in potential and that the anodic current at the upper potential limit of 1.43 V increases by a factor of ~2 between 26 and 80 °C. The charge passed in the anodic process was determined by integration of the area under the voltammogram on the positive-going and subsequent return scans. This charge arises from Reactions 2 and 3 and hence the total anodic charge Q_a is equal to $(3x + 15y)F$ coulomb, where x and y are the number of moles of pyrite oxidized in Reactions 2 and 3, respectively.

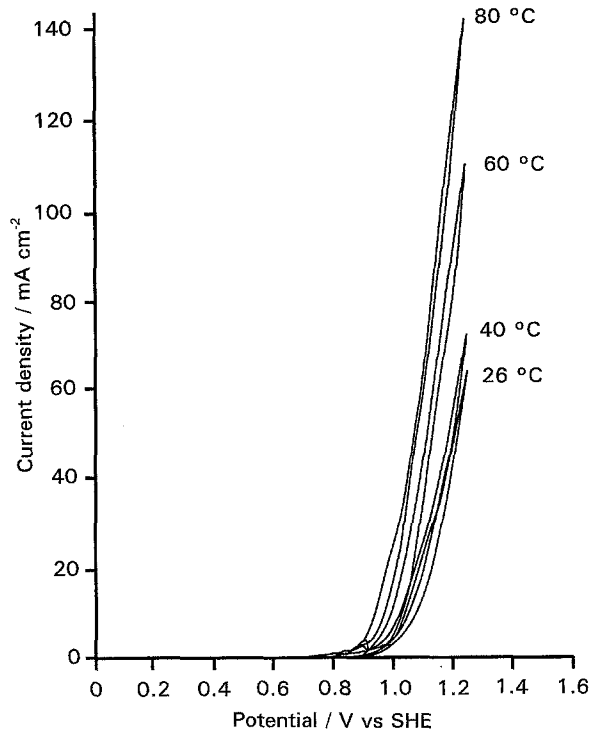

Fig. 2. Anodic sections of voltammograms for a pyrite electrode in 0.22 mol dm^{-3} nitric at 26, 40, 60 and 80 °C. Scans at 20 mV s^{-1} taken in the positive-going direction from near the rest potential and reversed at 1.23 V in each case.

Voltammograms were recorded at each temperature for potential cycles taken in the positive-going direction from close to the rest potential to different upper potential limits. Figure 3 shows the negative potential region of the subsequent negative-going scans for experiments carried out at 60 °C, and the following positive-going scan. The cathodic peak arises from reduction of sulphur by Reaction 4. The subsequent positive-going scan provides a measure of the current due to nitric acid reduction and hence the charge due to Reaction 4 can be obtained by integrating the cathodic charge between 0.2 and −0.4 V on the negative-going scan and subtracting the cathodic charge on the return scan integrated over this potential range. The cathodic charge determined in this way, Q_c, is equal to $4xF$ coulomb, since oxidation of pyrite by Reaction 2 produces

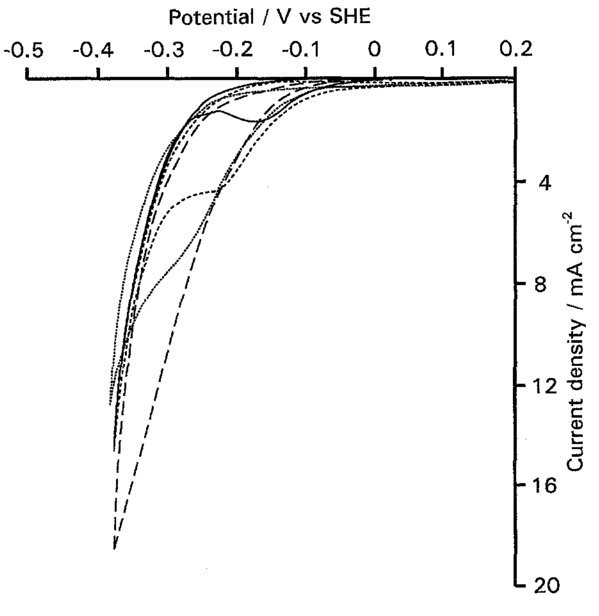

Fig. 3. The low potential region of cyclic voltammograms for a pyrite electrode at 60 °C taken initially in the positive-going direction from near the rest potential and reversed at (——) 1.03, (----) 1.13, (....) 1.23 and (– – –) 1.33 V. Scan rate 20 mV s^{-1}.

Table 1. Moles of sulphur and sulphate produced by electrochemical oxidation of pyrite in nitric acid on potential scans at 20 mV s^{-1}

Upper potential limit /V vs SHE	*26 °C*		*40 °C*		*60 °C*		*80 °C*	
	10^{-8} Moles cm^{-2} of Pyrite							
	S^0	SO_4^{2-}	S^0	SO_4^{2-}	S^0	SO_4^{2-}	S^0	SO_4^{2-}
0.82			1.1	0.2			2.2	1.5
0.92	0.53	0.69	1.8	1.4			2.3	5.7
1.02	1.7	2.6	2.5	8.9	2.5	9.4	6.4	24
1.12	3.9	19	4.5	21	7.2	40	15	73
1.22	4.7	52	7.3	56	11	83	16	215
1.32	4.1	107	5.4	103	14	212	11	310
1.42	2.6	196	2.8	185	1	335	3.3	426
1.52			2.4	245				

two S atoms. The percentage of the moles of pyrite oxidized to sulphur is equal to $100x/(x+y)$, which can be shown to be given by $1500Q_c/4(Q_a + 3Q_c)$.

Voltammograms for scans reversed at different upper potential limits and for a range of temperatures were analysed by the above procedure. The charges passed in oxidizing pyrite to sulphur and sulphate are presented in Table 1 in terms of mol cm^{-2} of pyrite. The percentage of pyrite oxidized to sulphur for each potential limit and temperature is given in Fig. 4. It can be seen that the relative formation of sulphur is independent of temperature and approaches zero at ~1.5 V. This potential is the same as that found at 25 °C by Biegler and Swift [8]. The absence of a variation with temperature confirms the suggestion made by those authors that the relative formation of sulphur and sulphate in the oxidation of pyrite at any particular potential varies to an insignificant extent with increase in temperature. This must reflect a similar activation energy for Reactions 2 and 3.

The potential at which the formation of sulphur becomes negligible, viz., 1.5 V, is chemically inaccessible in the nitric acid oxidation system. The overall process is one of reaction with oxygen and hence the mixed potential operating is limited to the reversible value for oxygen reduction. Thus, to eliminate sulphur, it is necessary to devise conditions in which the oxidation of sulphur to sulphate occurs at an acceptable rate through either the use of elevated temperatures or the addition of a catalyst.

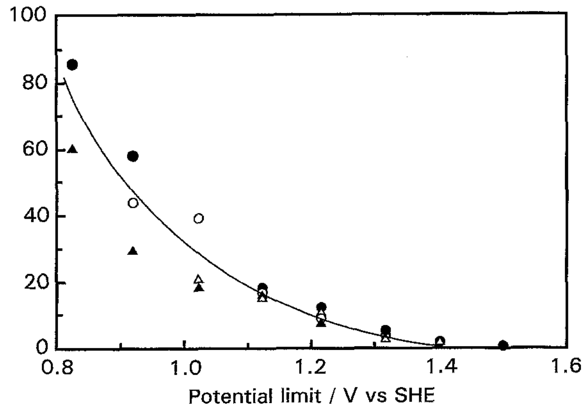

Fig. 4. Dependence of moles of pyrite oxidized to sulphur as a percentage of the total moles of pyrite oxidized on potential cycles at 20 mV s^{-1} as a function of the upper potential limit of the scan: (○) 26, (●) 40, (△) 60 and (▲) 80 °C.

At present, developers of commercial processes counteract elemental sulphur formation by operating at a temperature of 185 °C to enhance the kinetics of sulphur oxidation. It may require four times the reaction residence time to oxidize elemental sulphur at this temperature than it does to react the sulphide mineral itself [5].

It can be seen from Fig. 3 that the peak potential for reduction of sulphur shifts to more negative potentials as the upper potential limit is increased. If the scan were taken to higher upper potential limits than 1.52 V, separation of the charge due to Reaction 4 from that arising from reduction of nitric acid became difficult because there was insufficient difference in the potentials at which the two processes occur. This was not important in the present work since the charge due to sulphur deposition relative to that for sulphate formation was quite small at 1.52 V. For example, at 40 °C, the charge passed in sulphur formation at this potential was 1.41 mC and that for sulphate was 533 mC.

Changes in peak potentials on voltammograms can arise from an increase in the amount of reacting species present on the surface. This cannot explain the results reported here since a shift is observed even when there is little difference in the quantity of sulphur being reduced (e.g., Fig. 3 and Table 1). Thus, the behaviour must be ascribed to a change in the nature of the sulphur with variation in the potential range covered by the positive-going scan.

This conclusion is consistent with previous findings that the sulphur formed initially in the oxidation of pyrite may not be in the elemental form, but in a precursor, metastable state. X-ray photoelectron spectroscopic studies have been carried out [16] on the oxidation of pyrite in a range of media, including 2 mol dm^{-3} acid solution that was 95% HCl and 5% HNO_3. The S(2*p*) binding energy indicated that the sulphur product layer formed in the mixed acid included a range of environments between elemental sulphur and pyrite. It was suggested that oxidation of pyrite initially results in a metal-deficient pyrite layer and, when multilayers of a sulphur product are present, 'sulphur/sulphur (polysulphide-type) linkages are formed that allow iron atoms to influence a number of overlaying sulphur atoms'. Raman spectroscopic studies [17] of the products of anodic oxidation of pyrite also indicated the formation of polysulphides together with elemental sulphur in the potential range 0.65 to 1.25 V. The present studies would also suggest a change in the nature of the sulphur product with change in potential.

It seems quite possible that the oxidation products formed during the preoxidation of pyrite could be more reactive than elemental sulphur in its stable S_8 configuration. While the matter awaits further elucidation, this observation suggests there may be scope for refractory gold researchers to improve the kinetics of nitric acid preoxidation by identifying methods to oxidize the metastable sulphur species before it proceeds further to its stable form.

4. Conclusions

(i) The proportion of pyrite oxidized to sulphur (as opposed to sulphate) on a potential scan decreases with increase in potential, varying from about 70% at 0.82 to a negligible value at 1.5 V.

(ii) The proportion of sulphur formed at each potential is independent of temperature in the range studied, viz., 26 to 80 °C.

(iii) The peak potential for the cathodic reduction of sulphur shifts to more negative values as the upper potential limit of the scan is increased. This indicated a change in the nature of the sulphur product with the potential of formation.

(iv) Some elemental sulphur will always be formed under conditions obtainable in nitric acid preoxidation of pyritic refractory gold ores. To avoid the presence of sulphur in the final product, conditions need to be identified under which elemental sulphur, or the precursor metastable sulphur species, is oxidized to sulphate.

Acknowledgements

This work was funded by CSIRO/University of South Australia and CSIRO/University of Adelaide Collaborative Research Grants. The authors wish to thank Professor D. F. A. Koch, Professor F. Lawson and Dr Y. Ramprakash of Monash University and Dr B. O'Neil of the University of Adelaide.

References

[1] H. von Michaelis, 'Innovations in Gold and Silver Recovery', Randol International, Golden CO (1992).
[2] K. E. Sobel, K. A. Foo, J. C. Whellock and J. H. Canterford, in 'Randol Gold Forum', Vancouver (1992), pp. 4102–4107.
[3] G. Van Weert, K. J. Fair and A. H. Aprahamian, 2nd Int. Gold Conf., Vancouver, Canada, 7–9 Nov. (1988).
[4] A. W. Morrison, L. E. Robinson and N. M. Anderson, 'Randol Gold Forum', Squaw Valley CA (Sept. 1990), pp. 185–190.
[5] R. L. Leonard, K. S. Christensen and P. A. Dawson, 'Randol Gold Forum' Squaw Valley, CA (Sept. 1990), pp. 191–199.
[6] L. K. Bailey and E. Peters, *Can. Metall. Q.* **15** (1976) 333.
[7] T. Nagai and H. Kiuchi, *Nippon Kogyo Kaishi* **91** (1975) 547.
[8] T. Biegler and D. A. Swift, *Electrochim. Acta* **24** (1979) 415.
[9] R. T. Lowson, *Chem. Rev.* **82** (1982) 481.
[10] R. E. Meyer, *J. Electroanal. Chem.* **101** (1979) 59.
[11] I. C. Hamilton and R. Woods, *ibid.* **118** (1981) 327.
[12] T. Biegler, D. A. J. Rand and R. Woods, *ibid.* **60** (1975) 151.
[13] Y. Ramprakash, D. F. A. Koch and R. Woods, *J. Appl. Electrochem.* **21** (1991) 531.
[14] R. G. Bates, Determination of pH, Theory and Practice', John Wiley, New York (1964), 435 pp.
[15] E. Peters and H. Majima, *Can. Metall. Q.* **7** (1968) 111.
[16] A. N. Buckley and R. Woods, *Appl. Surf. Sci.* **27** (1987) 437.
[17] S. B. Turcotte, R. E. Benner, A. M. Riley, J. Li, M. E. Wadsworth and D. M. Bodily, *J. Electroanal. Chem.* **347** (1993) 195.