Journal of Thermal Analysis, Vol. 18 (1980) 147–154

A TG/MS AND DTA STUDY OF THE OXIDATION OF PENTLANDITE

J. G. DUNN and C. E. KELLY

Department of Chemistry, Western Australian Institute of Technology
Perth, Western Australia

(Received March 7, 1979)

The oxidative behaviour of natural pentlandite $(FeNi)_9S_8$ has been studied by thermogravimetry (TG) and differential thermal analysis (DTA) in a dynamic oxygen atmosphere (0.2 l min^{-1}) over the temperature range 20–1000°. Gaseous products were analysed by a coupled quadrupole mass spectrometer. The reaction products at various intermediate temperatures were characterised by X-ray diffractometry and chemical analysis. A reaction sequence has been deduced, in which in the temperature range 460–700° pentlandite breaks down with the formation of Fe_2O_3, $NiSO_4$, NiO, NiS and $NiFe_2O_4$; $FeSO_4$ was also formed but decomposed above 640°. Beyond 700° NiS was completely oxidised, and $NiSO_4$ decomposed slowly. Another sulphide phase, possibly $Ni_{3\pm x}S_2$, was formed at 740° and completely oxidised at 790°, and above 800° $NiSO_4$ decomposed completely leaving only Fe_2O_3, NiO and $NiFe_2O_4$ as stable products.

In two earlier studies members of this group have reported on the oxidation of synthetic forms of pyrrhotite [1] and millerite [2] as preliminary work leading to this present paper. Pentlandite $(NiFe)_9S_8$ is a primary nickel mineral of great economic importance. During smelting processes, floated pentlandite concentrate is mixed with suitable fluxes and then the iron component selectively oxidised and separated to produce a nickel matte. A review of the literature indicates that although work has been reported on the effect of heat on pentlandite in inert atmospheres [3–5] little detailed knowledge is available for oxidising conditions.

During the oxidation of a complex sulphide, two major processes have been identified.

(a) The formation of protective coatings on the surface of the mineral particle which may govern the extent of reaction, through inhibition of gaseous diffusion to the reactive sulphide. The ability of oxide layers to protect inner core material during the oxidation of pyrrhotite [1,6] and millerite [2] has been noted, and sulphate formation has also been shown to inhibit the sulphation of manganese oxides [7].

(b) The preferential diffusion, in binary sulphides, of one cation toward the oxygen-oxide or oxygen-sulphate interface which results in preferential oxidation. This has been shown to occur in roasted pentlandite minerals [8], where after a 30 minute roast at 685° the inner core material contained only 2.4% iron, whilst the outer core was iron rich. The ability of nickel ions to diffuse into pyrrhotite structures even at quite low temperatures (275–500°) has also been demonstrated [9].

So far Ni_3S_2, Ni_7S_6 and pyrrhotite have been identified in roasted pentlandite [8] although it has subsequently been found that Ni_7S_6 cannot exist above 575° [10] and hence it may have formed from a nonstoichiometric unquenchable form of Ni_3S_2 [11].

The purpose of this work is to attempt a detailed study of the oxidation of pentlandite over the temperature range ambient to 1000° and to deduce a reaction scheme. Of particular interest is the formation of unwanted minor byproducts such as nickel ferrite $NiFe_2O_4$.

Experimental

Oxidation runs were followed on a Stanton Redcroft TR 1 thermobalance modified to receive upflowing gas. Samples of about 250 mg were spread as thin layers in silica dishes, and heated at 600° hr^{-1} in a gas flow of 0.2 l min^{-1}. The TG was also used to heat 250 mg lots of pentlandite to selected temperatures between 530–850°, and the products quench cooled in air prior to qualitative analysis by XRD using a Siemens type F diffractometer. These samples were also analysed for soluble metal salts by boiling the sample gently in water, and then determining the iron and nickel values by atomic absorption analysis. It was assumed that the only soluble salts present were sulphates.

DTA runs were carried out using a Stanton Redcroft DTA attachment, with samples of about 25 mg contained in platinum dishes. An equal weight of calcined alumina was used as a reference material, and heating rates and gas flow rates were identical to those of the TG experiments.

An AEI Quad 160 quadrupole mass spectrometer was used for evolved gas analysis. The TG-MS system has been described previously [12].

The Nepean pentlandite was separated from gangue material by use of a Franz magnetic separator, and was estimated by optical microscopy to be better than 95% pentlandite. The major impurities were pyrites and pyrrhotite. Electron probe microanalysis gave values of 24.6 atomic % Fe; 27.9 atomic % Ni; and 0.3 atomic % cobalt. A DTA curve under N_2 showed a single peak at 610 ± 3°, which was identical to a previously quoted value for pentlandite [13].

Results and discussion

An inspection of the TG and DTA curves for pentlandite in oxygen shows many similarities to the curves obtained in studies on pyrrhotite [1] and millerite [2], and hence some of the reaction assignments are made by analogy.

Figure 1 shows the DTA curves for two samples of pentlandite heated in oxygen (1a) and air (1b) The exotherm at 790° and the endotherm at 830° appear to be independent of oxygen partial pressure, but the exotherms at 575° and 725° in figure 1a both changed in an air atmosphere. The effect of oxygen partial pressure is further demonstrated in the TG curves (figure 2a in oxygen, figure 2b in air) where the weight changes in air are less significant than in oxygen. The maxima in the DTG curve (figure 2a) show clearly the weight gain, and three major weight losses. The shoulders and gradients of the DTG curve also indicate that other reactions are taking place in concert with these major reactions.

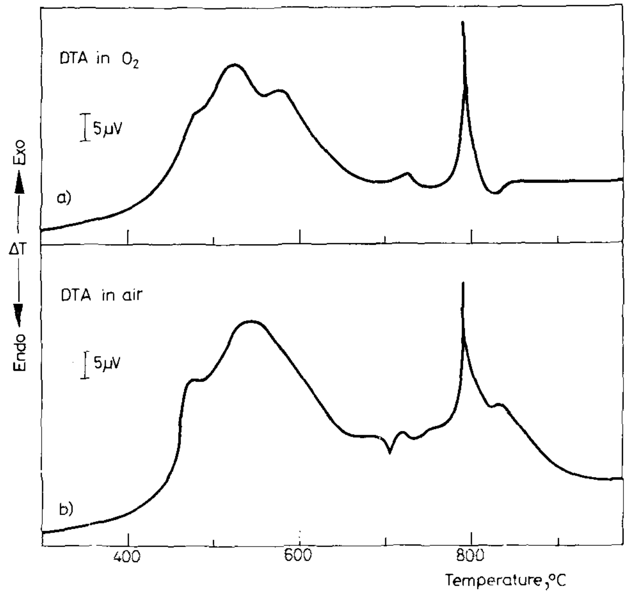

Fig. 1. DTA curves of pentlandite

Figure 2c is the MS trace obtained from the sample heated in oxygen (figure 2a). The peaks representing sulphur dioxide emissions can be correlated with the weight losses in the TG curve, and also the peaks in the DTA curve.

The results obtained from X-ray diffraction and chemical analysis are given in Tables 1 and 2.

Apparent TG weight gains below 460° are caused by buoyancy effects, and the real weight gain beyond 460° (figure 2a) can be attributed to the formation of $FeSO_4$ and $NiSO_4$ which although difficult to detect by X-ray diffraction (see Table 1) were confirmed by chemical analysis (see Table 2). The analysis values also indicate that $FeSO_4$ forms at a faster rate than $NiSO_4$. This weight gain continued smoothly until 550°, when an inflection in the TG curve indicated a lower rate of weight increase. At this stage in the DTA (figure 1a) an exotherm was apparent peaking at 520° and an SO_2 emission was evident in the MS results (figure 2c). Species detected by XRD at 530° were NiS, Pn1, Pn2 and Fe_2O_3.

The appearance of NiS as a major phase suggests that under-oxidising conditions the breakdown of Pn1 is substantial with the formation of FeS as well as NiS and leaving only minor quantities of Pn1 and Pn2. The oxidation of FeS by preferential diffusion of Fe^{2+} to the particle surface would account for the formation of Fe_2O_3, and by comparison with earlier work [1] the exotherm at 520° is assigned

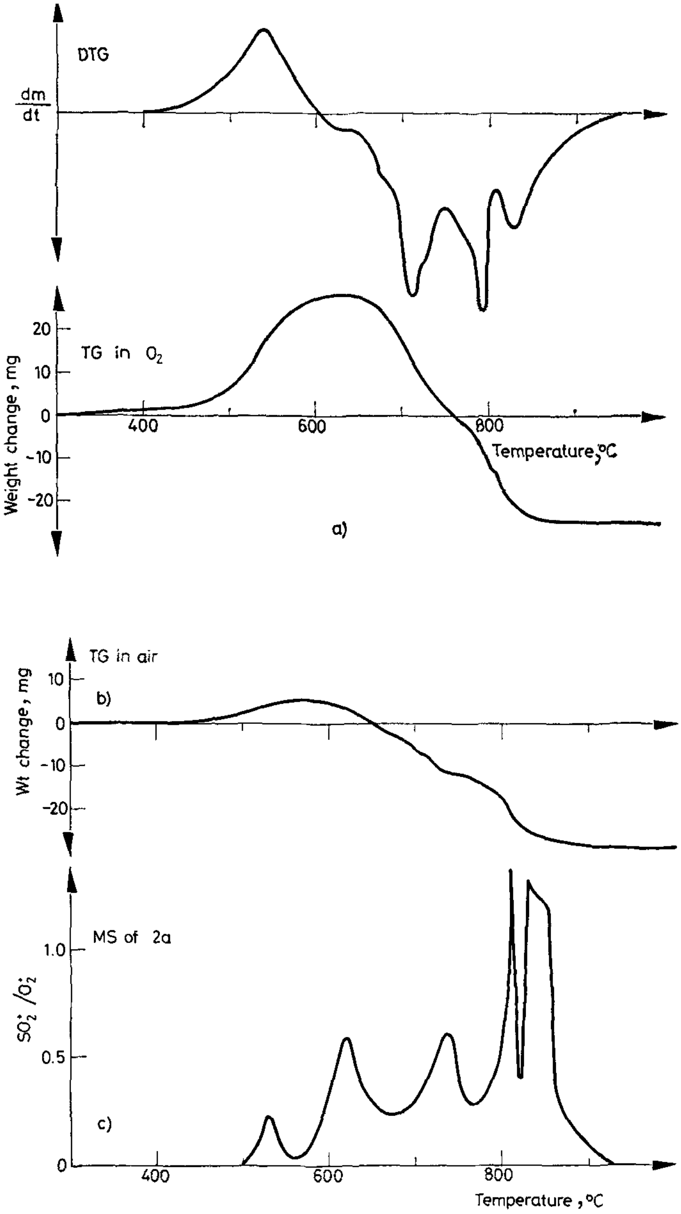

Fig. 2. TG, DTG and MS curves of pentlandite

to this reaction.

$$2\,FeS + 3.5\,O_2 \rightarrow Fe_2O_2 + 2\,SO_2$$

Some direct oxidation of NiS and FeS also occurs to form the respective sulphates, but the bulk of NiS remains protected by oxide and sulphate coatings.

NiS and Pn2 were also formed when Pn1 was heated in N_2 to 575°, although only partial decomposition of Pn1 occurred and no FeS was detected.

The most likely reaction to cause the exotherm at 575° in figure 1a is the oxidation of the Pn2 phase, since NiO and $NiFe_2O_4$ were detected by XRD in a sample quenched from 610°. An SO_2 emission is also evident in the MS results peaking at 620°. The higher temperature of this emission relative to the DTA peak may be because of the larger sample size used in the TG work compared to the DTA work;

Table 1

XRD analysis of rapidly quenched samples of oxidised pentlandite

Species detected	Temperature prior to quenching, °C						
	530	610	650	700	760	780	850
NiS	× ×	× ×	× ×	× ×			
Pn1	×	×	×	×			
Pn2	×	×					
Fe_2O_3	×	× ×	× ×	× ×	× ×	× ×	× ×
$NiSO_4$		×	×	×	×	×	
$FeSO_4$		×	×	×			
NiO		×	×	×	×	× ×	× ×
$Ni_xFe_{3\pm x}O_4$		×	×	× ×	× ×	× ×	× ×
$Ni_{3\pm x}S_2$						×	

× × indicates major phase based on XRD line intensity.

Pn1 refers to natural pentlandite, $(NiFe)_{9\pm x}S_{8\pm y}$.

Pn2 refers to a pyrrohite-like crystal structure that forms on heating Pn1 and has the composition $Fe_{8\pm x}Ni_{8\pm y}S_{16\pm z}$ [14].

Table 2

Analytical results for the determination of soluble Fe and Ni salts in quenched oxidised pentlandite samples

Sample temperature, °C	% Fe	% Ni
Pentlandite 25	0.01	0.01
530	2.00	0.53
610	7.38	1.72
650	4.00	2.81
700	1.00	5.01
760	0.09	3.31
800	0.04	2.80

the sensitivity of this peak to oxygen partial pressure has already been demonstrated.

$$Pn2 \rightarrow NiFe_2O_4 + NiO + Fe_2O_3 + SO_2$$

This assignment is supported by three experiments. Firstly pentlandite held isothermally in oxygen at 575° showed NiS, $NiFe_2O_4$ and Fe_2O_3 as major phases, with Pn1, $NiSO_4$, $FeSO_4$ and NiO as minor phases. Hence Pn2 had been completely oxidised. Secondly when intimate physical mixtures of NiS and FeS (1 : 1) were heated together in oxygen to 1000° no $NiFe_2O_4$ species was detected; similarly heated mixtures of NiO and FeO produced no evidence of $NiFe_2O_4$. This suggests that the ferrite must be formed from an iron-nickel compound rather than by reaction between separate species.

The TG showed a continuing weight gain to 630°, and chemical analysis on a sample quenched from 610° showed that the $FeSO_4$ content was at a maximum, whilst the $NiSO_4$ content was still increasing. The weight loss commencing at 640° is due to the decomposition of $FeSO_4$, as previously found [1] and supported by chemical analysis. A broad endotherm centred at 720° and assigned to the decomposition of $FeSO_4$ [1] was not apparent in this work (figure 1a). The complete oxidation of Pn2 also occurred between 610–650°. Under equilibrium conditions and an inert atmosphere both Pn1 and Pn2 are unstable above 610° [3], but under the dynamic conditions of 10° min^{-1} used in the present DTA work Pn1 persisted up to 700°.

Beyond 715° a steady weight loss was evident up to 775°. A small exotherm in the DTA curve at 740° correlated with an SO_2 emission in the TG-MS results at 735°. XRD results from a sample quenched from 760° indicated the disappearance of NiS, Pn1 and $FeSO_4$, with the appearance of a sulphide phase which had an XRD pattern similar to Ni_3S_2.

The presence of Ni_3S_2 would be indicative of the unquenchable compound $Ni_{3\pm x}S_2$, and this interpretation is favoured for the following reasons. The breakdown of Pn1 above 600° in an inert atmosphere has been previously shown to yield $Ni_{3\pm x}S_2$ and Pn2 [14]. In the roasting of pentlandite, it has also been shown that little iron remains in the kernal at 685° [8]. Further, the DTA curve for the oxidation of pentlandite bears a remarkable resemblance to the DTA curve for the oxidation of NiS above 750° [2], where obviously there is no possibility of forming a Fe-Ni sulphide phase. Hence it is tentatively suggested that between 700–740° Pn1 breaks down to form $Ni_{3\pm x}S_2$ and Pn2, the immediate oxidation of the latter contributing to the DTA peak and SO_2 emission between 730–740°. This suggestion is supported indirectly by the XRD results, which showed that Ni_2FeO_4 had reached its maximum concentration relative to previous temperatures.

The other major event in this temperature range is the disappearance of NiS, which is most likely to occur by simple oxidation, as previously suggested for millerite oxidation [2].

$$NiS + 1.5\,O_2 \rightarrow NiO + SO_2$$

The remaining $FeSO_4$ also decomposed in this temperature range and $NiSO_4$ also began to decompose. The major species present at 760° were Fe_2O_3 and $NiFe_2O_4$.

At 790° a sharp exotherm in the DTA curve corresponded with a rapid weight loss in the TG curve between 775–805° and a rapid emission of SO_2. These results are considered to arise from the rapid oxidation of $Ni_{3\pm x}S_2$, since this phase reacts between 780° and 850° (Table 1). The $Ni_{3\pm x}S_2$ phase has an incongruent melting point in the region of 800° [9] which explains its rapid oxidation.

$$Ni_{3\pm x}S_{2(s)} \rightarrow Ni_{3\pm x}S_{2(l)} \xrightarrow{O_2} 3NiO + 2SO_2$$

A further endotherm at 830° correlates with a weight loss commencing at 805° in the TG and a large emission of SO_2 peaking at 840°. These effects are associated with the decomposition of $NiSO_4$.

The various reactions can be summarised as:

< 460°	Pn1 → Pn2 + NiS + FeS
460–640	$FeS + 2\ O_2 \rightarrow FeSO_4$
460–715	$NiS + 2\ O_2 \rightarrow NiSO_4$
520*	$2\ FeS + 3.5\ O_2 \rightarrow Fe_2O_3 + SO_2$
575*	$Pn2 + O_2 \rightarrow Ni_2FeO_4 + SO_2 + NiO + Fe_2O_3$
640–760	$2\ FeSO_4 \rightarrow Fe_2O_3 + (2\ SO_2 + 0.5\ O_2)$
700–740	$Pn1 \rightarrow Ni_{3\pm x}S_2 + Pn2$
	$Pn2 + O_2 \rightarrow Ni_2FeO_4 + SO_2$
	$NiS + 1.5\ O_2 \rightarrow NiO + SO_2$
775–805	$Ni_{3\pm x}S_2 \xrightarrow{O_2} NiO + (SO_2 + 0.5\ O_2)$
>800	$NiSO_4 \rightarrow NiO + (SO_2 + 0.5\ O_2)$

* In these cases the reaction temperature range is difficult to determine from the curves, and the DTA peak temperature alone is quoted.

Because of the complexity of this system, some of the reaction assignments must be considered as tentative.

*

We wish to thank Dr. W. Barker (CSIRO) for the sample of pentlandite and valuable information, Dr. B. O'Conner (Physics) for XRD work, and Messrs. K. Oliver, B. Sturman and I. Twaddle (Chemistry) for technical assistance.

References

1. T. Kennedy and B. T. Sturman, J. Thermal Anal., 8 (1975) 329.
2. J. G. Dunn and C. E. Kelly, J. Thermal Anal., 12 (1977), 43.
3. G. Kullerud, Carnegie Inst. Wash. Year Book, 62 (1962) 174.

4. A. J. Naldrett, J. R. Craig and G. Kullerud, Econ. Geol., 62 (1967) 826.
5. K. C. Misra and M. E. Fleet, Econ. Geol., 68 (1973) 518.
6. A. V. Vanyukov, Chem. Abstr., 84 (1976) 63030 q.
7. T. R. Ingraham and P. Mauriar, Trans. Met. Soc. AIME, 242 (1968) 2039.
8. P. G. Thornhill and L. M. Pidgeon, J. Metals, 9 (1957) 989.
9. W. E. Ewers, Proc. Australasian Inst. Min. Met., 241 (1972) 19.
10. G. Kullerud and R. A. Yund, J. Petrol., 3 (1962) 126.
11. G. Kullerud, Carnegie Inst. Wash. Year Book, 58 (1958) 161.
12. T. Kennedy and I. W. Twaddle, ANZ 3rd conf. Mass. Spect. Canberra, 1975.
13. G. Kullerud, Can. Mineral., 7 (1963) 353.
14. A. P. Likhachev and Y. A. Brauer, Dokl. Akad. Nauk. USSR, 186 (1969) 154.

Résumé — On a étudié, par thermogravimétrie (TG) et par analyse thermique différentielle (ATD), en atmosphère dynamique d'oxygène (0.21 min^{-1}) et dans l'intervalle de températures allant de 20 à 1000°, le comportement de la pentlandite $(FeNi)_9S_8$ vis-à-vis de l'oxydation. On a analysé les produits gazeux formés avec un spectromètre de masse quadrupole couplé. On a caractérisé les produits de réaction à diverses températures intermédiaires par diffractométrie des rayons X et par analyse chimique. On en a déduit une séquence de réaction, dans laquelle la pentlandite se décompose dans l'intervalle 450—700° avec formation de Fe_2O_3, $NiSO_4$, NiO, NiS et $NiFe_2O_4$; $FeSO_4$ se forme également, mais se décompose au-dessus de 640°. Au-dessus de 700° NiS est complètement oxydé, et $NiSO_4$ se décompose lentement. Une autre phase sulfurée, probablement $Ni_{3\pm x}S_2$ se forme à 740° et est oxydée complètement à 790°. Au-dessus de 800°, $NiSO_4$ se décompose completèment ne laissant que Fe_2O_3, NiO et $NiFe_2O_4$ comme produits stables.

Zusammenfassung — Das oxidative Verhalten von natürlichem Pentlandit $(FeNi)_9S_8$ wurde durch Thermogravimetrie (TG) und Differentialthermoanalyse (DTA) in einer dynamischen Sauerstoffatmosphäre (0.21 min^{-1}) im Temperaturbereich 20—1000° untersucht. Die gasförmigen Produkte wurden durch ein gekoppeltes vierpoliges Massenspektrometer analysiert. Die Reaktionsprodukte bei verschiedenen Zwischentemperaturen wurden durch Röntgendiffraktometrie und chemische Analyse charakterisiert. Es wurde eine Reaktionssequenz abgeleitet, bei welcher Pentlandit im Temperaturbereich von 450 bis 700° unter Bildung von Fe_2O_3, $NiSO_4$, NiO, NiS und $NiFe_2O_4$ zersetzt wird; $FeSO_4$ wurde auch gebildet, wurde aber bei Temperaturen über 640° zersetzt. Über 700° wurde NiS vollständig oxidiert und $NiSO_4$ langsam zersetzt. Eine weitere Sulfidphase, möglicherweise $Ni_{3\pm x}S_2$ wurde bei 740° gebildet und bei 790° vollständig oxidiert. Über 800° wurde $NiSO_4$ vollständig zersetzt, wobei nur Fe_2O_3, NiO und $NiFe_2O_4$ als stabile Produkte zurückblieben.

Резюме — Было изучено окислительное поведение природного пентландита $(FeNi)_9S_8$ с помощью термогравиметрии и дифференциального термического анализа в динамической атмосфере кислорода (0.2 1 мин$^{-1}$) в области температур 20—1000°. Газообразные продукты анализировались квадрупольным масс-спектрометром. Продукты реакции при промежуточных температурах были охарактеризованы рентгеновской дифрактометрией и химическим анализом. Выведена последовательность реакций. В области температур 450—700° пенталандит расщепляется с образованием Fe_2O_3, $NiSO_4$, NiO, NiS и $NiFe_2O_4$. При этом также образуется $FeSO_4$, разлагающийся выше 640°. NiS выше 700° полностью окисляется, и $NiSO_4$ — медленно разлагается. Другая сульфидная фаза, возможно состава $Ni_{3\pm x}S_2$, образуется при 740° и полностью разлагается при 790°. Выше 800° полностью разлагается $NiSO_4$ и остаются в качестве стабильных веществ только Fe_2O_3, NiO и $NiFe_2O_4$.