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THE INFLUENCE OF ROASTING TEMPERATURE  
UPON GOLD RECOVERY FROM A REFRACTORY GOLD ORE.

A thesis submitted as partial requirement for a  
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Head

ABSTRACT  
SUMMARY

The results of this investigation indicate that the gold in the cyanide tailings of refractory gold calcines is occluded in fused or recrystallized iron oxide particles formed during roasting. These high temperature particles cannot be prevented by controlling the roasting atmosphere or by maintaining a low furnace temperature.

The above conclusions have been reached following a microscopic examination of calcines produced at various furnace temperatures with different atmospheres, and a comparison with calcines produced by decomposing samples of completely sulphated concentrate under such conditions that the maximum particle temperature varied between 650 C and 1100 C. This comparison showed that the particle temperature during a normal roast is several hundred degrees higher than the furnace temperature. An approximate relationship between the two is established for roasting the "refractory" arsenical gold concentrate examined during this investigation.

The unavoidable high particle temperatures occurring in furnace roasts are not upheld by theory since calculated radiation and convection losses exceed the heat generated. Rate of reaction and rate of oxygen diffusion calculations, however, do explain the failure of controlled atmospheres to give low particle temperature roasts at moderate furnace temperatures where the reaction is not diffusion controlled.

Because high particle temperatures could not be prevented during any furnace roast, and because low particle temperatures are essential for complete gold extraction by cyanidation, aqueous medium oxidation under high oxygen pressures was studied. Gold recoveries from calcines produced by this means was over 98% compared with 80% from furnace calcines. It

was shown that a medium with a high hydroxyl concentration gives adequate and rapid oxidation of the sulphides by increasing the chemical driving force by the oxygen-hydroxyl half cell potential.

### ACKNOWLEDGEMENT

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THE INFLUENCE OF ROASTING TEMPERATURE  
UPON GOLD RECOVERY FROM A REFRACTORY GOLD ORE.

OBJECT OF INVESTIGATION

Pyritic and arsenical ores containing sub-microscopic gold have long been regarded as refractory requiring special treatment to free the gold for solution by cyanide. The sulphides are usually roasted to free the gold and the calcines cyanided. This investigation was undertaken to determine why this treatment seldom yields gold recoveries of over 90%.

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## INTRODUCTION

This work is intended to explore some of the suggestions made by Mr. Haszard<sup>1</sup> and Mr. Norwood<sup>2</sup> in their investigations of the roasting of auriferous flotation concentrates.

To date general agreement on refractory gold concentrates and their treatment stresses the following points:

1. Gold occurs in elemental form in a very fine division, as solid solution in the pyrite or arsenopyrite lattice<sup>3,4</sup>.
2. A low particle temperature during roasting is essential if the resulting calcine is to give high gold extraction by cyanidation.

While agreement exists on the above points, no one has maintained a low particle temperature during a roast or measured the individual particle temperature. Obtaining a low particle temperature oxidation and measuring the temperature, therefore, formed the principal objectives of this investigation.

From a comparison of roasting and cyanidation tests on many refractory gold ores the following points appear:

1. The more finely divided the gold the more refractory the ore.
2. The more refractory the ore the greater the dependence of gold recovery upon particle temperature during the roast.

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1 Haszard, N. I., The Condition of Refractory Gold in Lake View and Star (Kalgoorlie) Ore, Australasian Institute of Mining and Metallurgy, No. 108, 1937.

2 Norwood, A., Roasting and Treatment of Auriferous Flotation Concentrates, Australasian Institute of Mining and Metallurgy, No. 116, 1939.

3 Edwards, A., Texture of the Ore Minerals, Australasian Institute of Mining and Metallurgy (Inc.), 1947, P.93.

4 Ginziro Kuranti, Synthetic Study of Gold-Bearing Pyrite, Sueyokwai-Si, 10, 419-424, 1941. Chemical Abstracts, 35, 3563, 1941.



To date strong evidence indicates that the gold is locked up by recrystallized or fused iron oxide during the roast. According to Mellor<sup>5</sup> two crystalline forms of ferric oxide exist, an  $\alpha$  ferric oxide stable at low temperatures, and a  $\beta$  ferric oxide stable at high temperatures. The transformation temperature for this change has been reported as occurring between 678 C and 1320 C. Mellor also reports ferromagnetic ferric oxide with the cubic lattice of magnetite transforming at 700 C into paramagnetic hematite with a rhombohedral lattice. In addition the iron-oxygen diagram shows  $\text{Fe}_2\text{O}_3$  transforming to magnetite and oxygen at 1450 C, the oxygen pressure required to prevent this transformation being in the hundreds of atmospheres<sup>6</sup>. Opposed to these chemical changes is the mechanical locking of the gold by incipient fusion of the iron oxide. Giving weight to the suggestion that the gold is occluded by  $\text{Fe}_2\text{O}_3$  decomposing to dense  $\text{Fe}_3\text{O}_4$  is the change of ochres during roasting, where the color darkens with increasing roasting temperature from yellow through red to black, while the specific gravity gradually increases.

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<sup>5</sup> Mellor, J. M., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 13, Longmans Green and Co., 1928, p. 787.

<sup>6</sup> White, J., The Physical Chemistry of Open Hearth Slags, The Iron and Steel Institute, 1944, p. 614.

## EXPERIMENTAL WORK

To reduce the number of variables during this investigation the following standard cyanidation procedure was adopted:

1. One hundred grams of the calcine was washed for one hour with 500 ml of water in an open five-litre wide-mouth jar with ten small pebbles and revolving on rolls at 10 rpm. The calcine was then washed twice by decantation from two litres or by filtration on a buchner filter.
2. The washed calcine was returned to the original jar and cyanided on the above mentioned rolls for 24 hr with 500 ml of water, 0.5 g of NaCN, and 1.0 g of CaO.

### I. Description of Ore

The material used as a basis for the tests throughout this investigation was a flotation concentrate produced by Con Gold Mines Limited having the following analysis:

Au	= 1.63 oz per ton	Pb	= 0.80%
Fe	= 34.3%	Cu	= 0.30%
S	= 33.0%	Zn	= 3.00%
As	= 17.1%	Insoluble	= 8.30%
Sb	= 0.60%		

The uniform structure of the concentrate, principally arsenopyrite, is shown in Plate I. A microscopic examination at 1800 magnification showed no free gold.

The low gold extraction by cyanidation of the raw concentrate, shown in Table I, indicates the refractive character of this concentrate.

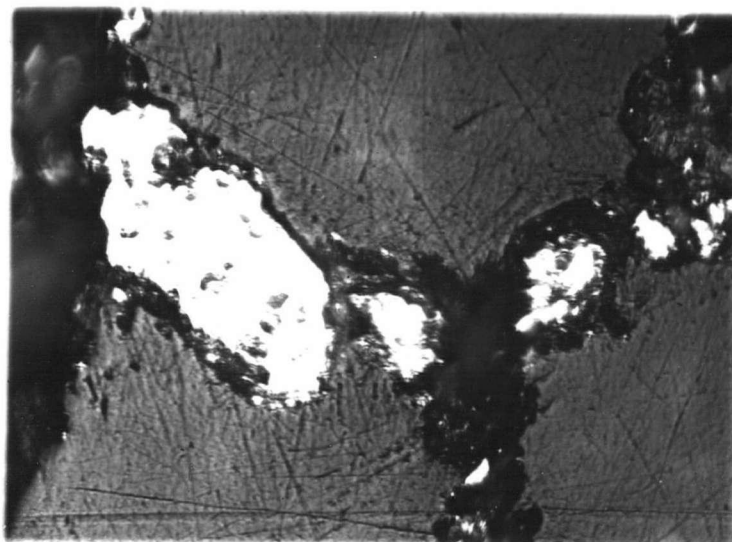


Plate I 375X  
Con Concentrate. Large, Uniform,  
Dense Arsenopyrite Grains with  
no Free Gold.

TABLE I

No.	Treatment	Gold Assay of Tailing (oz per ton)	Gold Extraction
C-1	None	1.28	21.5%
C-2	1.0 hr milling in laboratory pebble mill #	1.18	31.1%

#Note:

Mill Size = 7 in. by 7 in.  
Pebble Charge = 2765 g  
Mill Speed = 74 rpm  
Ore Charge = 1000 g  
Water = 400 ml

II. Apparatus

All furnace oxidation tests were made in silica trays sealed in a fire clay muffle, as shown in Figure I. The whole assembly was placed on two inch-high fire-clay blocks in a 13 kw Walker electric furnace. Thus it was possible to shield the surface of the charge from radiation

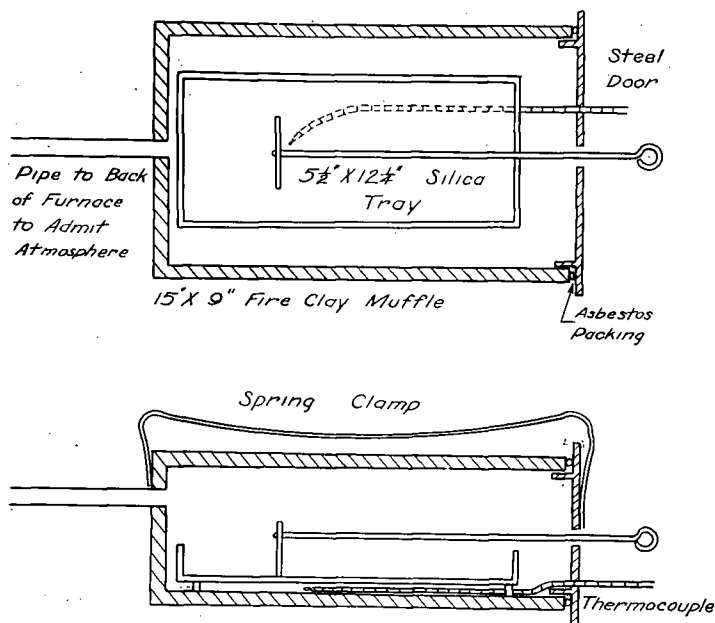


FIGURE I

from the furnace elements, and to maintain any desired atmosphere around the charge.

The aqueous media oxidation tests were made in the 1400 ml mechanically-agitated autoclave shown in Figure II.

### III. Experimental Work and Results

#### (A) Sulphide Oxidation

##### (a) Furnace Oxidation

Preliminary roasts showed that below 450 C Con concentrate roasted very slowly and above 450 C, despite constant rabbling, the charge glowed and the calcine bed temperature rose over 550 C. Gold extraction

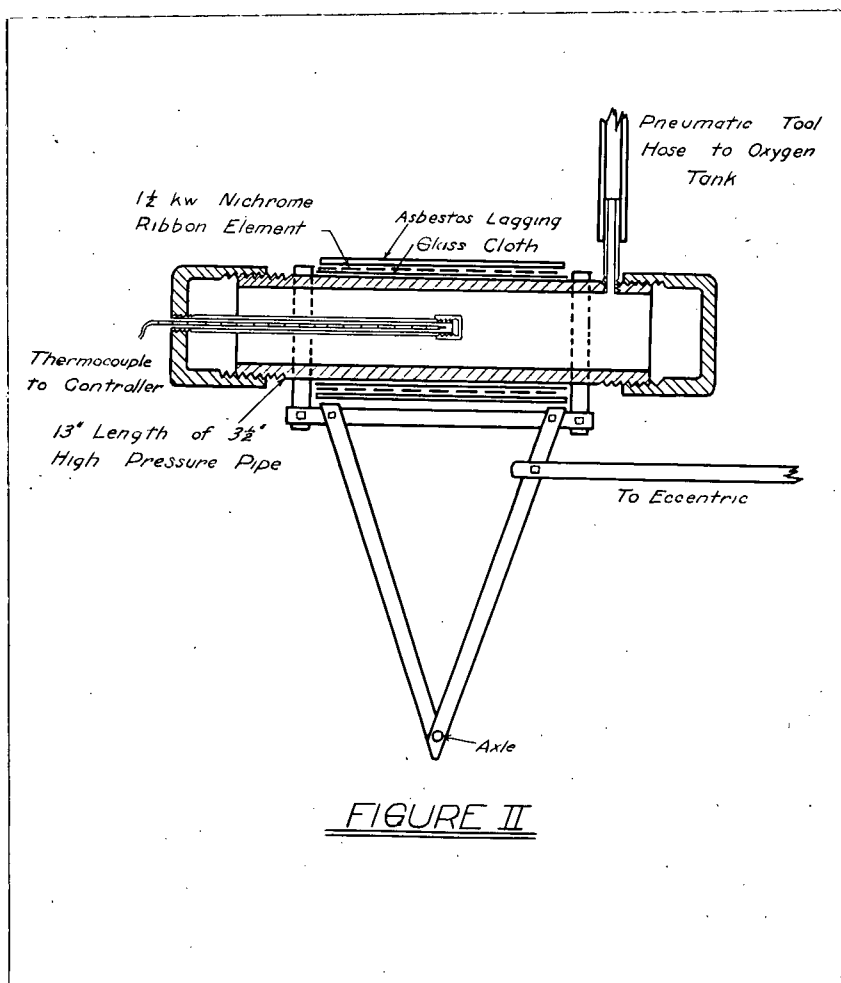


FIGURE II

from these calcines dropped from a maximum of 67% for a calcine produced in a furnace held at 450 C for 11 hr, to 16% for a calcine produced in a furnace where the temperature, initially 450 C, was raised 50 C every 30 min to a maximum of 750 C.

Because of these high initial roasting temperatures, the Con concentrate was heated under nitrogen at 600 C for one hour to distill off the arsenic as a mixture of  $AsS$  and  $As_2S_3$ . This treatment removed the arsenic as a possible cause of low gold extraction and increased the roasting rate of the concentrate at low temperatures by increasing its specific surface area. This distilled concentrate was used for all future furnace oxidation tests. The porous sulphide,  $FeS_{1.1}$ , containing 0.6%

to 0.8% arsenic and 31.8% to 33.1% sulphur is shown in Plate II.

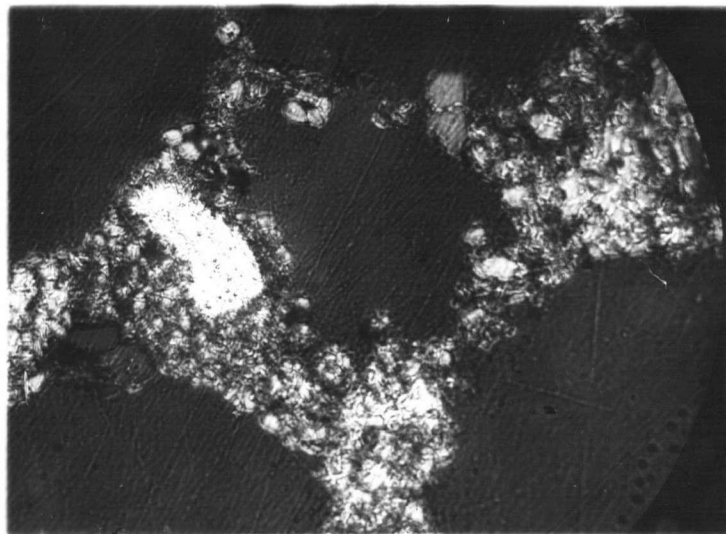
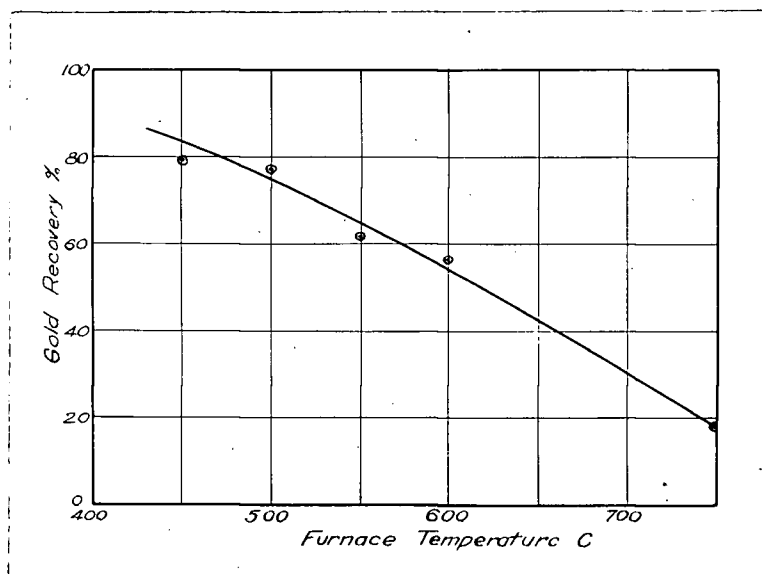


Plate II 375X  
 Distilled Con Concentrate. Shows Porous  
 Structure of Distilled Concentrate and  
 One Dense Particle of Undistilled  
 Arsenopyrite.

(i) Air Atmosphere Roasts

To determine the influence of temperature upon gold extraction the porous pyrrhotite from the distillation was roasted in the sealed muffle of Figure I with constant rabbling under an air atmosphere. During this series the initial furnace temperature was fixed at 400 C, the lowest temperature at which roasting would begin, and the final temperature was varied from 450 C to 750 C. During the roast the temperature was raised 50 C every 15 min to the maximum temperature, which was held until the evolution of sulphur dioxide ceased. The results of these tests are summarized on Graph I, and a few typical results are given in detail in Table II.



Graph I  
Effect of Furnace Temperature  
on Gold Recovery from Calcines  
Produced by Furnace Oxidation  
of Distilled Con Concentrate.

TABLE II

No.	Max. Temp.	Time at Max.Temp.	Calcine Assay		Gold Assay of Tailings (oz per ton)	Gold Extraction
			Sulphide Sulphur	Sulphate Sulphur		
C-44	---	---	32.3 %		1.08	45.0 %
C-53	450 C	3Hr	5.48 %	4.19 %	0.48	79.8 %
C-54	500 C	1.5Hr	4.68 %	1.30 %	0.54	76.6 %
C-47	550 C	0.5Hr	1.23 %	1.31 %	0.84	60.9 %
C-37	600 C	0.5Hr	1.98 %	1.86 %	0.98	56.2 %
C-34	750 C	0.5Hr	0.07 %	0.15 %	1.58	16.3 %

Note:

No. C-44 is the Con concentrate after heating under nitrogen for one hour at 600 C.

No. C-53 and C-54 showed no glowing particles during roasting.

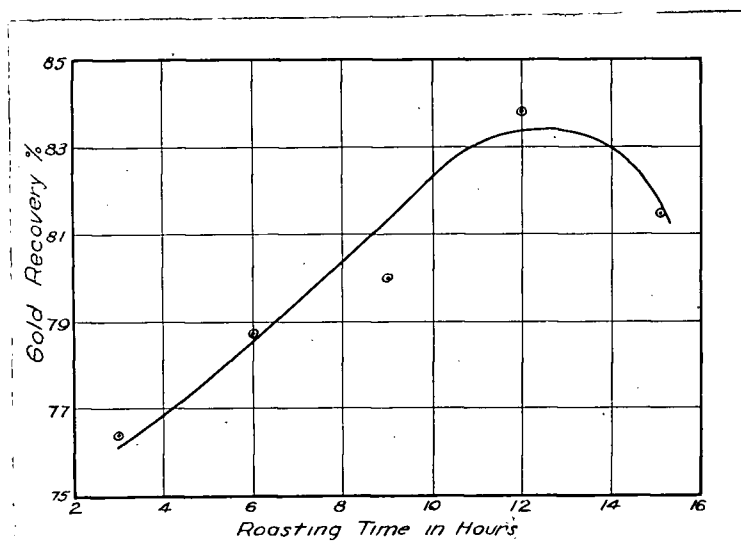
No. C-47 and C-37 glowed slightly during roasting.

No. C-34 glowed strongly during roasting.

From Graph I the complete dependence of gold recovery upon roasting temperature is obvious. Because of the exponential dependence

of roasting rate on temperature, the true particle temperature is much higher than shown on the abscissa of Graph I.

To study the influence of roasting time upon gold recovery a series of roasts was made in the sealed muffle under an air atmosphere at the optimum temperature of 400 C to 450 C found from the previous series. A plot of recovery against roasting time is shown in Graph II and a few typical results are given in detail in Table III.



Graph II  
Effect of Roasting Time at  
Optimum Temperature upon Gold  
Recovery from Calcine Produced  
by Furnace Oxidation of Distilled  
Con Concentrate.

TABLE III

No.	Time	Calcine Assay Sulphide Sulphur	Assay Sulphate Sulphur	Gold Assay of Tailings (oz per ton)	Gold Extraction
C-61		31.8 %		1.08	44.8 %
C-66-1	3 Hr	14.6 %	2.5 %	0.54	76.5 %
C-66-2	6 Hr	5.1 %	4.8 %	0.52	78.8 %
C-66-3	9 Hr	6.2 %	4.8 %	0.50	79.8 %
C-66-4	12 Hr	6.1 %	5.1 %	0.46	84.0 %
C-70	15 Hr	3.6 %	5.7 %	0.48	81.5 %



Note:

During these roasts no glowing of the sulphide particles occurred.

## (ii) Controlled Atmosphere Roasts

Controlled atmosphere roasts were investigated to determine if high particle temperature by flashing could be prevented by reducing the oxygen partial pressure over the sulphides. These low oxygen atmospheres were divided into two series, one having a high and the other a low sulphur dioxide content, to determine the influence of the sulphating roast, which has been claimed by many metallurgists to increase gold recovery from refractory ores. The results of this study are given in Table IV and Graph III.

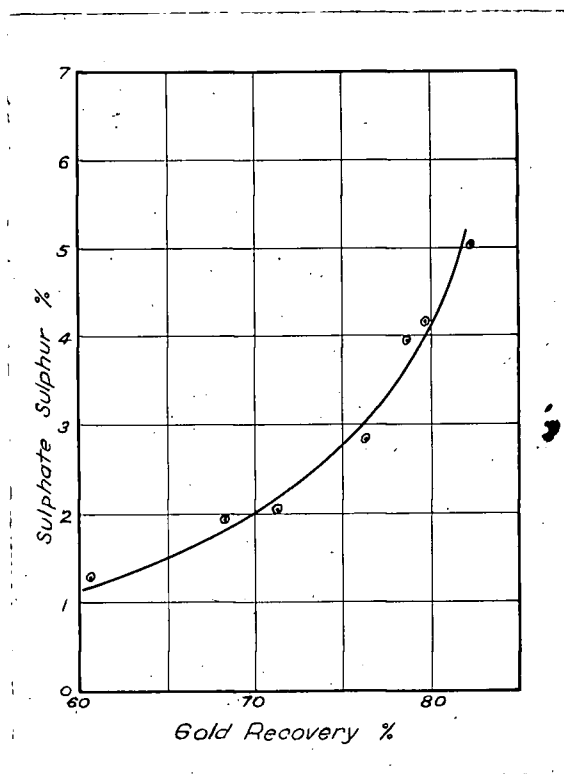
TABLE IV

No.	Max. Temp.	Time	Atmosphere O <sub>2</sub> SO <sub>2</sub>	Calcine Assay Sulphide Sulphur	Gold Assay Sulphate Sulphur	Gold Assay of Tailing (oz per ton)	Gold Extraction
C-50	450 C	2 Hr	14 %	17.6 %	2.75 %	0.52	77.0 %
C-52	450 C	4 Hr	14 %	4.4 %	3.97 %	0.50	78.7 %
C-49	450 C	7 Hr	14 %	3.89%	5.03 %	0.46	82.6 %
C-63	450 C	4 Hr	14 % 7.4 %	2.0 %	4.8 %	0.54	76.8 %
C-62	450 C	7 Hr	14 % 7.4 %	1.10%	5.52 %	0.54	76.0 %
C-64	450 C	9 Hr	14 % 7.4 %	0.80%	5.15 %	0.52	78.8 %

Note:

During these roasts no glowing of the sulphide particles occurred.

These low oxygen roasts, as shown by Table IV, did not raise gold recovery above that given by air atmosphere roasts at the same furnace temperatures. The sulphating roasts, similarly, did not improve recovery. The small amount of iron sulphate formed during these roasts implies that either sulphation at 450 C is very slow and incomplete, or that the particle temperature during the roast was above the decomposition temperature of



**Graph III**  
Influence of Sulphate Sulphur Content  
Upon Gold Recovery from Calcines Produced  
by Furnace Oxidation of Distilled Con  
Concentrate.

iron sulphate. This latter supposition finds support in nature where both ferric and ferrous sulphates are formed in atmospheres containing negligible amounts of sulphur dioxide. Thus the final sulphate content of a calcine under the conditions maintained during this series of experiments appears to be independent of the percent sulphur dioxide in the atmosphere but to depend upon the maximum particle temperature during the oxidation. If the sulphate sulphur is a record of the maximum particle temperature, the extreme sensitivity of gold recovery to particle temperature is shown by the large positive slope of Graph III.

#### (b) Aqueous Media Oxidation

Because of the impossibility of preventing high particle temperatures during a furnace roast, aqueous medium oxidation under high oxygen pressures was investigated. By such an oxidation the combination of low particle

temperature and high reaction rate is possible, because of the high oxygen pressure or driving force present and the high specific heat and intimate contact of the liquid medium with the sulphide particles. Thus local overheating of the sulphide particles is impossible.

Aqueous media oxidation of sulphides under high oxygen pressures has been reported by very few investigators<sup>7,8,9</sup>.

(i) Distilled Con Concentrate

Two hundred gram samples of distilled Con concentrate, C-92, which had been ground for one hour in the laboratory pebble mill to give C-101, were agitated in 500 ml of either alkali or ammoniacal solution under high oxygen pressures in the autoclave shown in Figure II. The resulting pulps were then filtered, washed, and cyanided as usual. The results of this work are given in Table V.

TABLE V

Aqueous Media Oxidation of Distilled Con Concentrate

No.	<u>Treatment in Autoclave</u>			Sulphide Sulphur In Calcines	Gold Assay of Tailings (oz per ton)	Gold Extraction
	Temp.	Time	<u>Oxygen Pressure (absolute)</u> <u>Liquid Initial</u> <u>Media Final</u>			
C-92				33.2 %	1.08	44.5 %
C-101				33.2 %	.96	49.9 %
C-97	90C	4Hr	47psi 13N NH <sub>4</sub> OH	NH <sub>4</sub> OH-Low 29.1 %	.28	83.8 %
C-98	90C	4Hr	47psi 13N NH <sub>4</sub> OH	NH <sub>4</sub> OH-Low 24.5 %	.08	95.5 %
C-105	150C	4Hr	115psi 13N NH <sub>4</sub> OH	NH <sub>4</sub> OH-0.3N 27.8 %	.90	53.3 %
C-106	150C	1Hr	115psi 12N NaOH	NaOH-2.5N 7.7 %	.16	92.4 %
C-107	150C	1Hr	115psi 12N NaOH	NaOH-1.7N 5.5 %	.08	96.2 %
C-108	150C	1Hr	115psi 12N NaOH	NaOH-0.2N 0.4 %	.04	98.0 %
C-109	150C	4Hr	115psi .35N NaOH	CaO-6.04N 27.6 %	.90	52.9 %

7 Bognar, A., Humid Oxidation of Sulphide Ores Under High Pressure, Magyar Mérnök Esiteszegylet Közlönye, 78, p.200-4, 1944. Chemical Abstracts, 7340<sup>a</sup>, 1947.

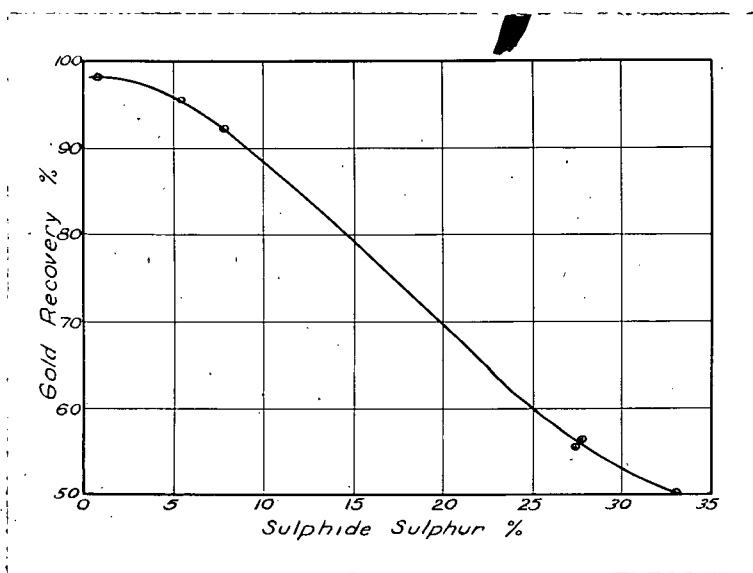
8 Tronev, V., and Bondin, S., Oxidation of Zinc Sulphide and Transference of Zinc into Aqueous or Alkali Solution Under Air Pressure, Compt.Rend.Acad. Sci., U.R.S.S., 23, 541-3, 1939.

9 Zvyagentsev, O., and Tronev, V., Oxidation of Copper Sulphide and Solution of Copper in Aqueous Solution Under Air Pressure, Compt.Rend.Acad. Sci., U.R.S.S., 23, 537-40, 1939.

Note:

1. To all times listed in Tables V and VI, except tests C-97 and C-98, must be added 0.5 hr to heat the autoclave, oxygen pressure 80 psi.
2. To all times listed in Tables V and VI, except tests C-97 and C-98, must be added 0.5 hr to cool the autoclave, oxygen pressure increasing from 115 psi to 170 psi, as the vapor pressure of water decreased on cooling.
3. Vapor pressure of 13 N aqua ammonia at 80 C = 20 psi.
4. Vapor pressure of 13 N aqua ammonia at 150 C = 110 psi.
5. Vapor pressure of water at 150 C = 70 psi.
6. To C-109 was added 140 g of CaO.

As seen by the high gold recoveries listed in Table V a low particle temperature oxidation has been obtained. Surprisingly, tests C-97 and C-98 gave high gold recoveries with low sulphur elimination, although the other calcines gave recoveries which depended upon the sulphur elimination as shown in Graph IV. Why tests C-97 and C-98 should lie so far off this graph has not been determined.



Graph IV  
Dependence of Gold Recovery upon  
Sulphide Sulphur Content for  
Distilled Con Concentrate decomposed  
by Aqueous Media Oxidation.

Apparently test C-105 did not oxidize because of the low oxygen partial pressure in the autoclave resulting from the high vapor pressure of aqua ammonia at 150 C.

The final ammonia concentrations have no significance because of vapor losses while emptying the hot autoclave.

(ii) Raw Con Concentrate

To determine if the dense arsenopyrite of the raw concentrate could be decomposed by aqueous medium oxidation, 200 gram samples of concentrate, after grinding two hours to give C-99-A, were treated as outlined in table VI.

TABLE VI

Aqueous Media Oxidation of Ground Con  
Concentrate C-99-A

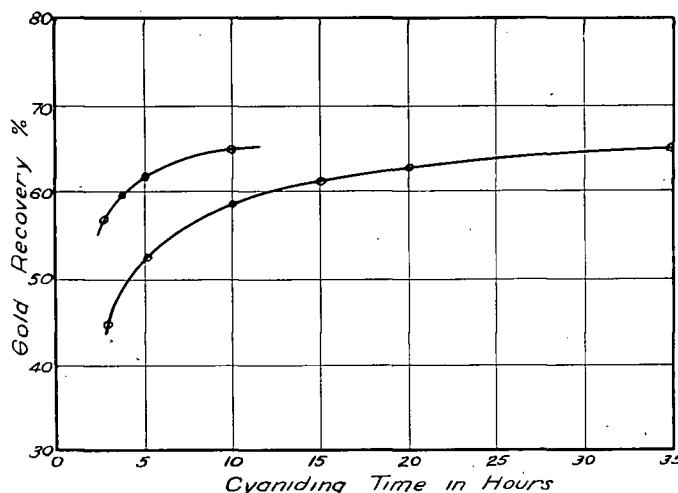
No.	Treatment in Autoclave			Media		Sulphide Sulphur in Calcine	Gold Assay of Tailings (oz per ton)	Gold Extraction
	Temp.	Time	Oxygen Press. absolute	Initial	Final			
C-99-A						33.0 %	1.16	31.2 %
C-99	80C	4Hr	47 psi	13N NH <sub>4</sub> OH	NH <sub>4</sub> OH-Low	29.8 %	1.06	35.1 %
C-100	80C	4Hr	47 psi	13N NH <sub>4</sub> OH	NH <sub>4</sub> OH-Low	29.1 %	0.96	40.1 %
C-110	150C	4Hr	115 psi	12N NaOH	NaOH-10N	27.6 %	0.38	76.5 %

These tests indicate that aqueous media oxidation of raw Con concentrate is much slower than for the distilled concentrate. This drop in reaction rate results from the small specific surface area of the raw concentrate compared to that of the distilled concentrate.

In this series of tests as for the aqueous media oxidation of distilled concentrate, one sample, C-110, gave high gold recovery with low sulphur elimination. In this series the irregularity occurs in the sodium hydroxide rather than the aqua ammonia medium. Hence the medium cannot be responsible for the phenomenon.

(iii) Combined Aqueous Media Oxidation and Pressure Cyanidation

Pressure cyanidation tests of a Con calcine, C-79, at 21 psi gauge oxygen pressure showed the cyanidation rate to be increased by the oxygen pressure, with no improvement in overall gold extraction. The result of this work is shown in graph V. A few tests were made, therefore, on



Graph V  
Effect of Oxygen Pressure  
upon Cyanidation Rate for  
Con Calcine C-79

distilled and raw concentrate to determine if the cyanidation rate could not be increased to equal the sulphide aqueous medium oxidation rate. Thus the gold would be dissolved in the autoclave as soon as it was freed from the sulphide. Such treatment, however, dissolved only about half the gold that a standard 24 hr cyanidation dissolved from the same calcines. Hence the cyanidation rate under 115 psi of oxygen can only be approximately half the oxidation rate of the sulphides.

(B) Study of Calcines

(a) Thermal Decomposition of Sulphated Con Concentrate

To substantiate the supposition that the gold is occluded by iron oxide and to determine the particle temperature during a normal roast,

completely sulphated distilled Con concentrate was decomposed at various temperatures. Several kilograms of distilled concentrate was completely sulphated with excess sulphuric acid, the excess acid being fumed off. This sulphated material was then decomposed by heating in a tube furnace under both oxygen and nitrogen atmospheres and the resulting calcine cyanided. In this way local overheating of individual particles, which always occurs during an ordinary roast, was prevented, the decomposition of iron sulphate being an endothermic reaction. The results of this work are given in table VII.

TABLE VII

No.	Max. Temp.	Time at Max.Temp.	Calcine Assay			Gold Assay of Tailing (oz per ton)	Gold Extraction	Calcine Appearance
			Fe <sup>+++</sup>	Fe <sup>++</sup>	S as SO <sub>4</sub>			
<hr/>								
	Sulphated							
C-69	Conc.		21.8%		22.8%			
C-71	650C	6 Hr	42.0%		8.0%	0.10	96.2%	Fluffy, Brick Red
C-76	875C	0.5 Hr	51.5%	0.5%	0.9%	0.10	95.8%	Darker than C-71
C-102	1000C	0.5 Hr	51.0%	1.1%	0.2%	0.48	75.6%	Dark Red
C-73	1100C	0.5 Hr	50.8%	1.8%	0.2%	0.96	50.7%	Very Dense, Black

In these results the atmosphere is not recorded since it did not influence the gold recovery. Once again the particle temperature appears as the factor governing gold extraction from calcines.

#### (b) Gold Nucleolation Experiments

Because the state of division of the gold is believed responsible for the refractory qualities of gold ores, the refractory degree of the ore should be reduced by nucleolation of the gold particles. Following the procedure of Burg<sup>10</sup>, such attempts were made by heating 125 g portions of raw Con concentrate under nitrogen in a sealed steel bomb for several hours

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<sup>10</sup> Burg, G., Natur des in den Pyriten nicht Sichtbar enthaltenen Goldes, Zestschrift fur praktische Geologie, February 1935.

at 600 C. The resulting calcines were then washed and cyanided. The results of this work are listed in Table VIII where they are compared with extractions from (a) raw concentrate, (b) concentrate ground for one hour in the laboratory pebble mill, and (c) distilled concentrate.

TABLE VIII

No.	Treatment	Gold Assay of Tailing (oz per ton)	Gold Extraction
C-1	None	1.28	21.5 %
C-2	1.0 hr grind in laboratory pebble mill	1.18	31.1 %
C-92	Distilled Concentrate	1.08	45.0 %
C-87	16 hr at 600 C under N <sub>2</sub> in bomb	1.34	35.1 %
C-88	24 hr at 600 C under N <sub>2</sub> in bomb	1.36	34.6 %
C-89	32 hr at 600 C under N <sub>2</sub> in bomb	1.36	34.2 %
C-90	47 hr at 600 C under N <sub>2</sub> in bomb	1.38	33.3 %

From the above results it is evident that the described treatment has only slightly increased gold extraction. Hence, the gold could not have been nucleolated, since nucleolated gold particles could be expected to cyanide readily. The slight increase in gold recovery after heating must result from the decrease in particle size shown by Plate III.

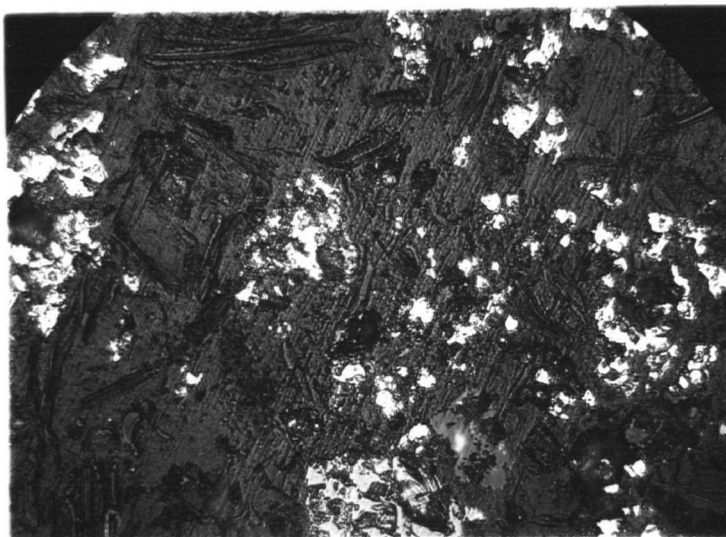


Plate III Tailing 1.38 oz per ton 375 X  
Calcine Cyanidation Residue C-90. Con Concentrate  
Heated 47 Hr in Sealed Bomb. Shows small grains  
of sulphide having little porosity.



(c) Microscopic Examination of Calcines

Three calcines produced by furnace oxidation of distilled concentrate to yield high, intermediate, and low gold extractions were microscopically compared with samples of sulphated distilled concentrate thermally decomposed at 650 C, 875 C, 1000 C and 1100 C. These three furnace calcines are shown in Plates IV to VI and the thermally-decomposed samples in Plates VII to X. The combination of low gold extraction and large iron oxide particles at high roasting temperatures is clearly shown by these plates.



Plate IV    Tailing 0.44 oz per ton    1000X  
Calcine Cyanidation Residue C-49. Distilled Concentrate  
Roasted at 400 C. The pores of much of the iron oxide  
are extremely small and the walls thin, although partial  
fusion has occurred to a considerable extent.

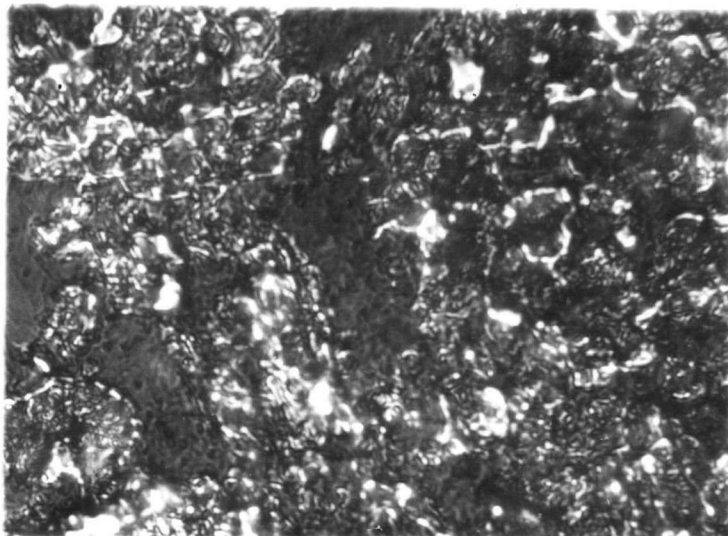


Plate V Tailing 0.84 oz per ton 1000X  
Calcine Cyanidation Residue C-47. Distilled Concentrate  
Roasted at 500 C. The pore walls are thicker than for  
C-49 and some grains show almost complete fusion around  
their boundaries.

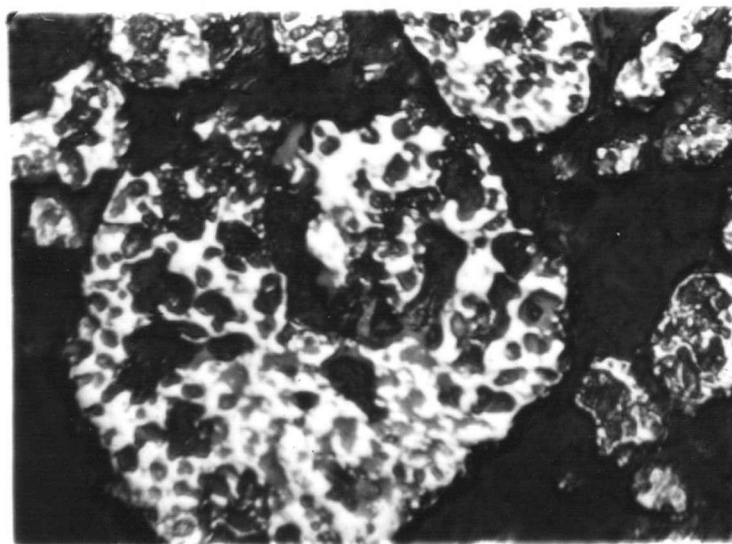


Plate VI Tailing 1.58 oz per ton 1000X  
Calcine Residue C-34. Distilled Concentrate Roasted at  
750 C. The pores are much larger than for C-49 or C-47  
while the walls are thick and continuous.

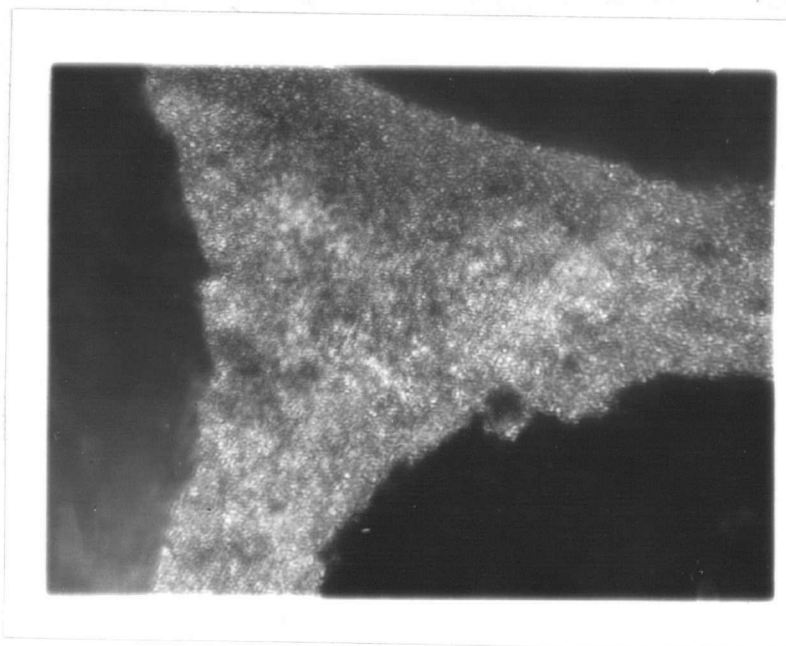


Plate VII Tailing 0.10 oz per ton 1800X  
Calcine Cyanidation Residue C-71. Sulphated Concentrate  
decomposed at 650 C. Particles are so fine that they  
cannot be resolved at 1800 magnification.

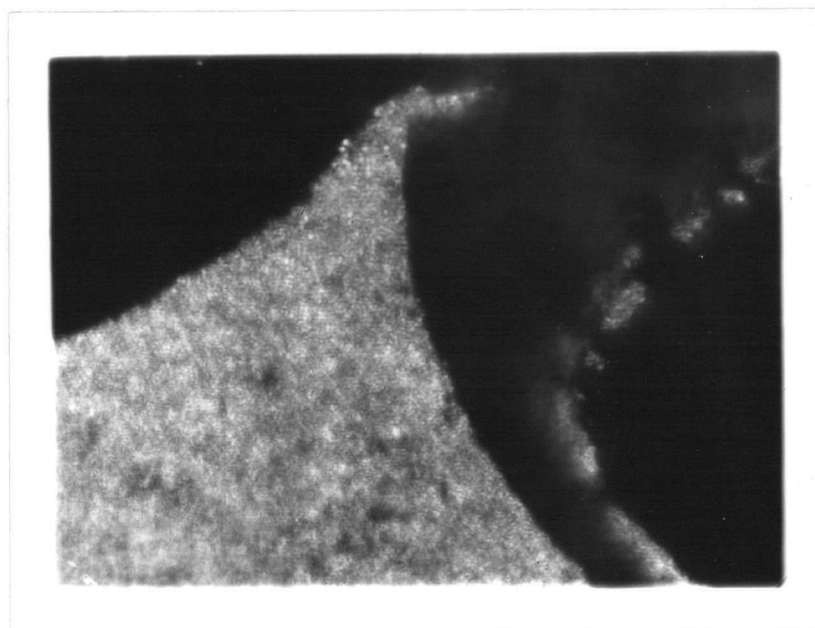


Plate VIII Tailing 0.10 oz per ton 1800X  
Calcine Cyanidation Residue C-76. Sulphated Concentrate  
decomposed at 875 C. Particles are very fine as in C-71.

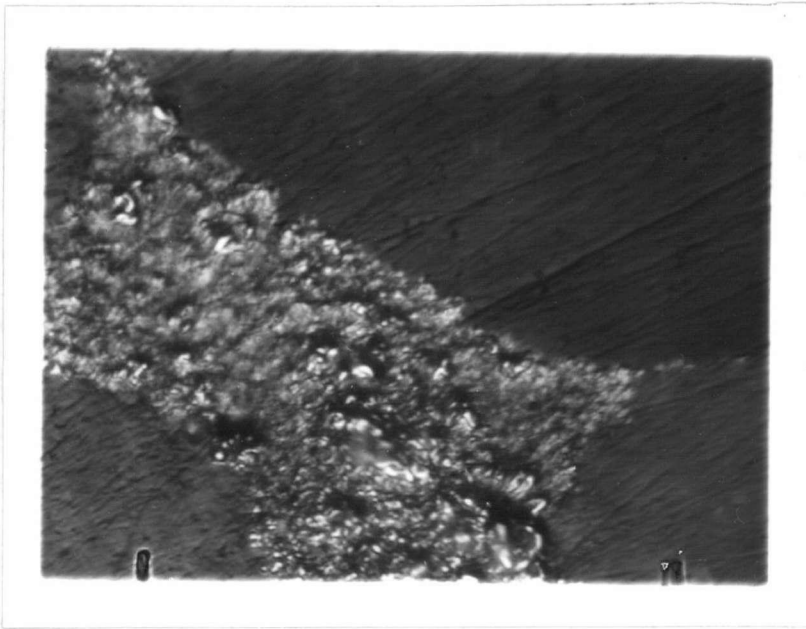


Plate IX Tailing 0.48 oz per ton 1000X  
Calcine Cyanidation Residue C-102, Sulphated Concentrate  
decomposed at 1000 C. Calcine particles have grown  
probably due to partial fusion of iron oxide.

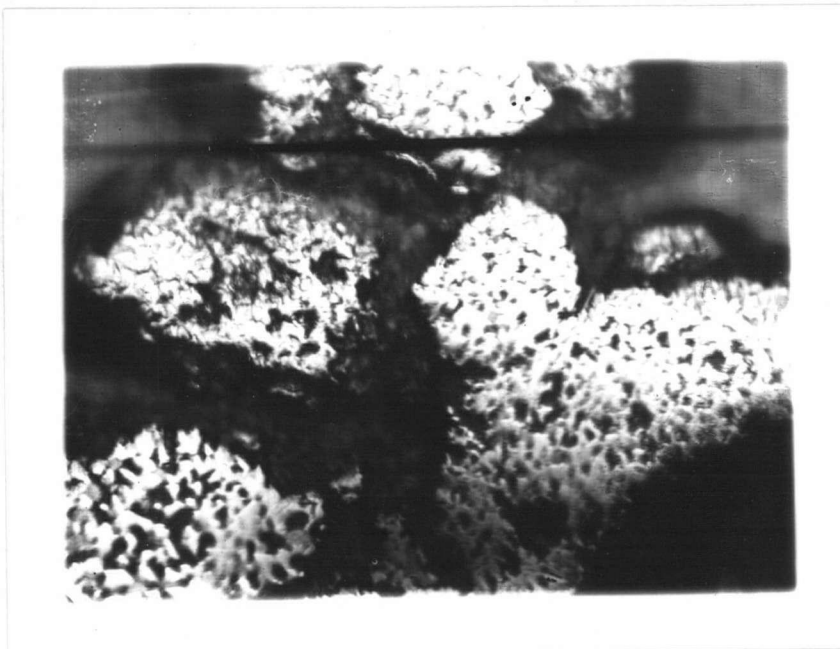


Plate X Tailing 0.96 oz per ton 675X  
Calcine Cyanidation Residue C-73. Sulphated Concentrate  
decomposed at 1100 C. Calcine particles have grown  
and increased in density with increasing temperature.

Once the gold has been coated by the partial fusion shown in the previous plates it cannot be freed by fine grinding nor by hydrochloric acid washes as shown in table IX. Throughout this work the influence of fine

TABLE IX

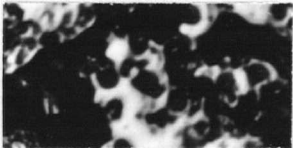
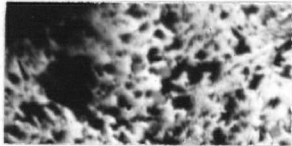

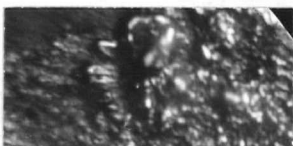
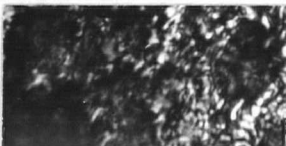
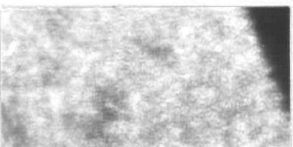
No.	Treatment	Gold Assay of tailing (oz per ton)	Gold Extraction
C-56	None	0.58	75.0 %
C-56-B	0.5 hr grind in pebble mill	0.56	75.8 %
C-56-C	1.0 hr wash in 1% HCl	0.56	77.4 %
C-56-D	1.0 hr wash in 2% HCl	0.56	77.4 %
C-56-E	1.0 hr wash in 5% HCl	0.58	76.6 %

Note:

C-56 was produced by roasting distilled concentrate at 450 C for three hours, to 1.29 % sulphide sulphur.

grinding upon gold extraction decreased as the quality of the calcine improved. This suggests that in a calcine yielding a high gold recovery the unextracted gold is locked in particles smaller than can be obtained by grinding.

Table III. Shows Relationship Between Particle and  
Furnace Temperature During A Roast of Distilled Con  
Concentrate

Series I Calcines Produced by Direct Roasting of Distilled Con Concentrate	Furnace Temp.	Particle Temp.	Series II Calcines Produced by Decomposing Sulphated Distilled Con Concentrate
	750C		
<u>C-34</u> <u>1000X</u> <u>Tailings = 1.58 oz./T</u> Evidence of greater fusion than in C-73		1100C	
	500C		<u>C-73</u> <u>675X</u> <u>Tailings = 0.96 oz./T</u> Evidence of considerable fusion and particle growth.
<u>C-47</u> <u>1000X</u> <u>Tailings = 0.84 oz./T</u> Evidence of greater fusion than in C-49 but less than in C-73		1000C	
	400C		<u>C-102</u> <u>1000X</u> <u>Tailings = 0.48 oz./T</u> Evidence of fusion similar to C-49
<u>C-49</u> <u>1000X</u> <u>Tailings = 0.44 oz./T</u> Evidence of fusion similar to C-102		875C	
			<u>C-76</u> <u>1800X</u> <u>Tailings = 0.10 oz./T</u> No evidence of fusion of particles

## DISCUSSION OF RESULTS

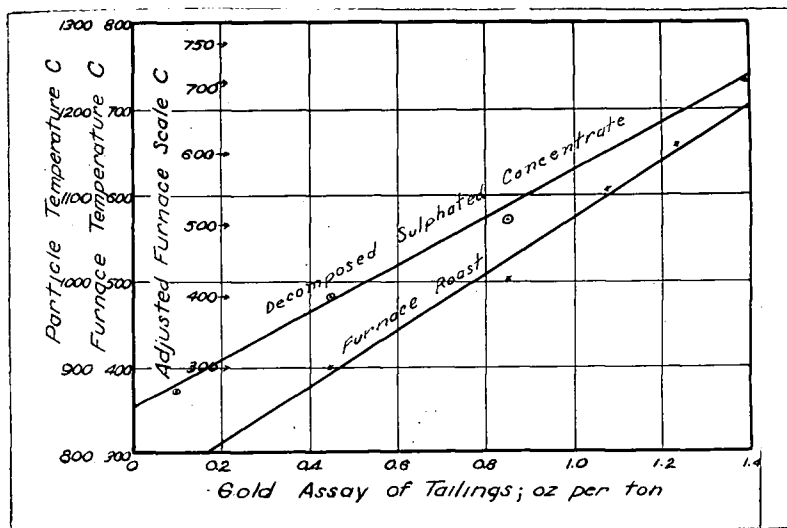
### I Furnace Oxidation

#### (A) Experimental Results

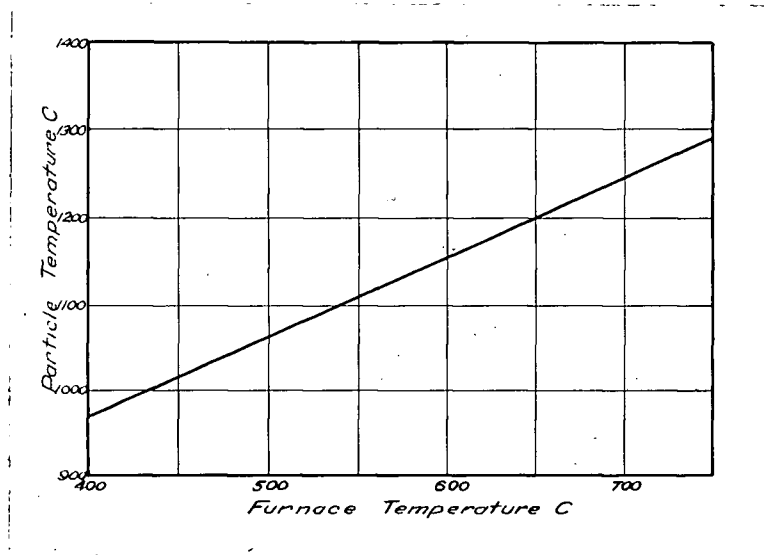
This investigation has clearly shown how gold extraction from the Con concentrate, as for most refractory sulphide gold ores, depends upon the maximum particle temperature during the roast.

In Figure III, opposite, the comparison of calcines produced by furnace oxidation of distilled concentrate and produced by thermal decomposition of sulphated concentrate shows that high particle temperatures during furnace oxidation cannot be prevented. The arrangement of the calcines in order of decreasing particle temperatures, and the known particle temperatures during decomposition of the sulphated concentrate gives an estimate of the maximum particle temperature during a furnace roast. This relationship is found by plotting in Graph VI. temperature against gold extraction for both the furnace calcines and the decomposed sulphated-concentrate calcines. The temperature scale of the furnace calcines is then adjusted to coincide with the plot for the decomposed sulphated concentrate. From the two temperature scales Graph VII is drawn relating the maximum particle temperature to the furnace temperature. These graphs are approximate but they provide an estimate of the particle temperature at any furnace temperature for the distilled Con concentrate roasted under the conditions previously described.

The failure of atmosphere controlled roasts to increase the gold recovery are surprising in view of the favorable results such roasts have given during other investigations. The low oxidation temperature required for high gold recovery from the Con concentrate is the apparent explanation for this failure.



Graph VI  
Effect of Temperature upon Tailing  
Assay for both Furnace Roasts of  
Distilled Con Concentrate and Thermally  
Decomposed Sulphated Concentrate.



Graph VII  
A Plot of Particle Temperature during  
a Furnace Roast against Furnace Temperature  
for the Distilled Con Concentrate.



### (B) Calculation of Heat Flow From Oxidizing Sulphide Particles

The experimental results of this investigation indicate that increased gold extraction from the Con concentrate can be obtained only by oxidizing the sulphides at lower particle temperatures than has been possible by roasting. When oxidation begins during a furnace roast, the particle temperature cannot be controlled because the heat generated by the reaction cannot be dissipated from the sulphide particles.

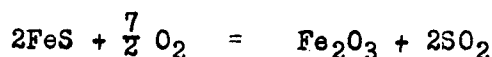
Radiation calculated with the surroundings at 450 C, an emissivity of one, a particle diameter of 0.0073 cm (200 mesh) and an area to diameter ratio of 10 is given by the following equation:

$$Q_r = 9.4 \times 10^6 \left\{ \left( \frac{T_2}{1000} \right)^4 - 0.274 \right\} \text{ cal per mole of FeS per sec. (a)}$$

From calculations which will be shown later the maximum likely roasting rate is given by the equation:

$$r = \sqrt{T_2} (2.84 \times 10^4) e^{-\frac{22500}{T_2}} \text{ moles of FeS per mole per sec}$$

The heat evolved by the reaction:



is given by:

$$\Delta H = -146,229 + 6.84T - 15.212 \times 10^{-3} T^2 \text{ cal per mole of FeS}$$

The combination of these expressions gives the following equation for the rate at which heat is generated by the oxidation of FeS:

$$Q_R = \sqrt{T_2} \left( 146,229 - 6.84T + \frac{15.212}{1000} T^2 \right) (2.835 \times 10^4) e^{-\frac{22500}{T}} \text{ cal per mole of FeS per sec (b)}$$

These results, compiled in Table X, indicate that at all particle temperatures radiation will dissipate the heat generated.

TABLE X

$T_2$ Particle Temp. (cal per mole FeS per sec)	$Q_R$ (Heat Generated) (cal per mole FeS per sec)	$Q_r$ (Heat loss by Radiation) (cal per mole FeS per sec)	$Q_c$ (Heat loss by Convection) (cal per mole FeS per sec)
500 C	3.6	$0.078 \times 10^7$	$0.019 \times 10^7$
700 C	12.4	$0.584 \times 10^7$	$0.085 \times 10^7$
1000 C	$3.3 \times 10^3$	$2.21 \times 10^7$	$0.22 \times 10^7$
1500 C	$6.6 \times 10^5$	$9.02 \times 10^7$	$0.501 \times 10^7$
2000 C	$1.4 \times 10^7$	$24.8 \times 10^7$	$0.763 \times 10^7$

Unfortunately the above results are invalidated by enclosing the roast in a fire clay muffle. Because the temperature gradient across the muffle walls is practically zero, the heat flow from the roasting bed by radiation and subsequent conduction through the muffle walls will be practically zero. Therefore, most of the radiated heat will be reflected back to the roasting bed.

It might be argued that the assumption that all the sulphide particles are free to radiate heat is invalid. This difficulty is overcome by considering that those particles which are not free to dissipate heat are not free to oxidize or generate heat since they are not receiving oxygen.

Heat flow by convection to the atmosphere is less than that by radiation since air is a good insulator because of the large mean free path of its molecules. Hence each sulphide particle may be assumed to be surrounded by an insulating air blanket.

Heat loss by convection from spheres is given by Langmuirs' equation:

$$Q_c = S(\phi_2 - \phi_1) \text{ watts per sphere}$$

Assuming, as before, a particle diameter of 0.0073 cm and taking Langmuirs' thermal conduction factors,  $\phi$ , for still air, the heat flow by convection is given by:

$$Q_c = (0.123 \times 10^7)(\phi_2 - 0.20) \text{ cal per mole}^{\text{of}} \text{FeS per sec}$$

Correcting the above equation for an extreme air velocity of 1000 cm per second increases the convection loss by 5.45 to give the results listed in Table X.

The calculations in Table X show that neither radiation nor convection will explain the high particle temperatures occurring during furnace oxidation, since heat flow by either mechanism exceeds the heat generated. Either the roasting rate equation or the heat transfer equations must be in error.

(C) Calculation of Sulphide Oxidation Reaction Rates

Diev and Karyakin<sup>11</sup> studied the roasting rates of FeS in oxygen-enriched air with the following conclusions:

1. At 500 C the rate of oxidation is independent of the oxygen pressure of the atmosphere.
2. Above 700 C the rate of oxidation is dependent upon the oxygen pressure of the atmosphere.

These measurements indicate that the oxidation of the FeS used by Diev and Karyakin is reaction rate controlled below 500 C and diffusion rate controlled above 700 C.

Because the distilled Con concentrate has the composition  $\text{FeS}_{1.1}$ , the above findings should be approximately true for this investigation. The roasting rate of distilled Con concentrate near 500 C is therefore independent of the atmosphere but depends exponentially upon the absolute temperature. Thus the heat liberated by the reaction and the particle temperature are practically impossible to control during a furnace roast, because of temperature gradients in the roasting bed. When the particle temperature reaches approximately 700 C, the reaction rate becomes equal to the oxygen diffusion rate to the sulphide interface and depends upon the oxygen pressure of the atmosphere. High particle temperatures and the accompanying low gold extractions are inevitable by such roasts, because of the combination of high reaction rate, high heat of reaction, and low specific heat of air.

This condition is shown by the following calculations based on two roasting rate measurements for FeS by Diev and Karyakin:

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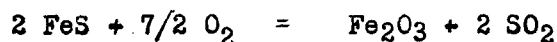
<sup>11</sup> Diev, N. P., and Karyakin, Yu. V., Roasting of Sulfides with Air Enriched with Oxygen, Journal of Applied Chemistry, U.S.S.R., 11, 1112-22, 1938.

1. At 500 C the roasting rate is reaction controlled and equals 0.0000238 moles per mole per second.
2. At 700 C the roasting rate in air is diffusion controlled and equals 0.000525 moles per mole per second.

From this data and the Arrhenius equation,  $K = Ae^{-E/RT}$ , and assumed activation energies of 25, 35, and 45 kilocalories per gram mole of FeS the oxidation rate when reaction rate controlled is estimated as shown in Graph VIII. This range of activation energies for FeS oxidation was selected for the following reasons:

1. The range 20 to 50 kilocalories per gram mole is given by Eyring<sup>12</sup> for the majority of chemical reactions.
2. The relation between activation energy and the temperature at which a reaction attains a measurable rate, as given by Hinshelwood<sup>13</sup>, yields a value of 45 kilocalories per gram mole.

Consider the reaction rate when diffusion controlled. The average diffusivity of oxygen through the stagnant nitrogen film and against the counter-diffusing sulphur dioxide may be estimated from the relationships developed by Gilliland<sup>14</sup> knowing only the molecular weights, molecular volumes, and concentrations of the individual gases. The oxygen concentration at the sulphide interface is zero, because the reaction is diffusion controlled. The sulphur dioxide concentration is assumed 12% by volume at the interface and zero in the gas stream. This gradient yields a sulphur dioxide diffusion rate 0.571 times that of the oxygen as demanded by the stoichiometric equation:




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12 Glasstone, S., Lardler, K., Eyring, H., The Theory of Rate Processes, McGraw-Hill Book Company, 1941.

13 Hinshelwood, C., The Kinetics of Chemical Change in Gaseous Systems, Clarendon Press, 1933, p. 121.

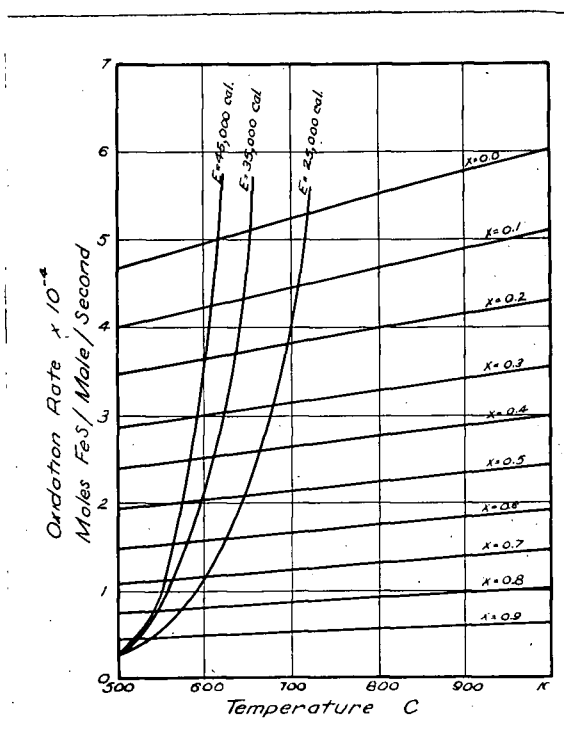
14 Gilliland, E. R., Industrial Engineering Chemistry, 26, 1934, p. 681.

As for the previous convection calculations a gas film 0.1 cm. thick is considered to surround each sulphide particle. The measured roasting rate for FeS of 0.000525 moles per mole per second at 700 C, gives the following oxidation rate equation when diffusion controlled:

$$r = \frac{6.38 \times 10^{-6} \sqrt{T} (1-X)^{2/3}}{1.379 - (1-X)^{1/3}} \text{ moles of FeS per mole per second}$$

X = fraction of the sulphide particle oxidized.

This equation is plotted on Graph VIII for various values of X.



Graph VIII  
Effect of Temperature upon Oxidation  
Rate of FeS when Chemical Rate Controlled  
and when Diffusion Controlled.

Graph VIII shows clearly that at low temperatures the oxidation rate is lower than the oxygen diffusion rate. At these temperatures the oxidation rate is independent of atmosphere composition. Similarly the graph shows that at high temperatures the diffusion rate or atmosphere composition controls the oxidation rate.

Graph VIII also indicates that as roasting proceeds diffusion controls the oxidation rate to lower temperatures. This mechanism explains the calcine structure shown by Plate V, where the surfaces of several particles are fused indicating a high initial roasting rate and the centres are unresolved at 1000 magnification indicating a low final roasting rate.

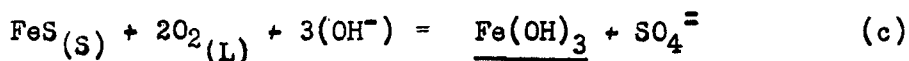
## II Aqueous Media Oxidation

A roast with low particle temperatures obtained by an aqueous medium oxidation gives complete extraction of the gold by cyanide solution which confirms the supposition that gold in cyanide tailings results from high particle temperatures. The oxidation in a liquid medium is increased to measurable rates at 150 C by the increased solubility of oxygen at high partial pressures. The oxidation rate is further increased by the restrictions placed upon the vibrations of the oxygen molecules by the medium. An oxygen molecule in solution whenever it approaches a particle collides many times with the sulphide surface rather than just once as would a gaseous oxygen molecule. Although the net movement of a molecule in a liquid is much slower than in a gas, the collision frequency is therefore approximately the same as for an equal oxygen concentration in a gas. Because of its high specific heat and intimate contact with the sulphide particles, the liquid medium prevents overheating or flashing of the particles during the oxidation.

A medium having a high hydroxyl ion concentration is essential for rapid and complete oxidation as shown by a comparison of the sulphide content of C-108 and C-109 and by the following calculations. At 25 C and 115 psi, oxygen solubility in the average 4N NaOH medium of C-108 and in the neutral medium of C-109 are  $1.0 \times 10^{-3}$  and  $9.6 \times 10^{-3}$  moles per litre respectively. At 150 C these concentrations are reduced by a factor of 0.61. The oxidation potential calculated at 25 C from these oxygen solubilities, free energy data, and the final ferric, sulphate, and hydroxyl ion concentrations

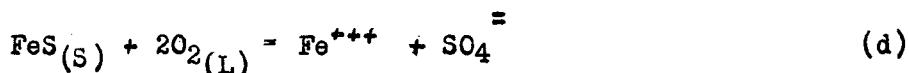
are as follows:

1. For the alkali medium reaction:



The driving potential = 1.2 volts.

2. For the neutral medium reaction:



The driving potential = 0.9 volts.

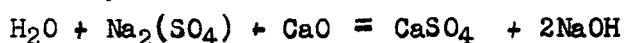
The above 0.3 volt difference is equivalent to the standard oxygen-hydroxyl half cell of 0.401 volts corrected for the concentrations of the reactants and products. Part of the difference between the 0.3 and 0.401 volts probably resulted from errors in the free energy values used.

Because of the slight oxidation occurring in the neutral medium either of two reactions is suggested:

1. The driving potential of 0.9 volts compared to 1.2 volts for the alkali medium gives a lower rate of reaction. This is unlikely, however, since the rate appears to be reaction controlled and should therefore depend upon temperature.
2. The true driving potential in the neutral medium may approach zero because of an overvoltage developed on the surface of the sulphide. This supposition is more likely since the FeS has a metal type lattice involving no electron exchange. The iron on oxidizing to the ionic state, in common with all metals, would evolve hydrogen and develop a hydrogen overvoltage.

The free energy calculations definitely show that the concentration difference in hydroxyl and ferric ions between the two media cannot account for the difference in oxidation potential. The free energy difference resulting from the hydroxyl and ferric ion concentrations being only 3700 calories compared to a total free energy change of -219,000 calories for reaction (c) and -164,000 calories for reaction (d).

The caustic used by the alkali medium reaction can be regenerated with lime by the reaction:



after filtering off the calcine.

The above calculations were made at 25 C rather than 150 C, because of the limited high temperature free energy data available. Since the change in free energy with temperature is likely to be of the same order for both reactions, the difference in oxidation potential between the two media at 150 C should not vary greatly from 0.3 volts.



### CONCLUSIONS

The following conclusions are drawn from this investigation:

1. Gold recovery by cyanidation from refractory ores is determined by the maximum particle temperature during a roast. The starting temperature, final temperature, and roasting speed do not affect gold recovery except as they affect the maximum temperature of the individual roasting particles.
2. Gold recovery from each calcine particle is determined by the degree to which some compound, probably iron oxide, imprisons the gold by incipient fusion or recrystallization.
3. A low temperature roast is obtained by oxidation of the sulphides in an alkali medium under high oxygen pressures. This oxidation gives a calcine in which all the gold is free and 100% soluble in cyanide solution. In the liquid medium, natural weathering or oxidation is thus obtained in as little as one hour for a porous sulphide.
4. A concentrated alkali solution is required to obtain a driving force during aqueous medium oxidation sufficient to give a measurable rate of reaction at low temperatures.
5. Neither hydrochloric acid washes nor extreme fine grinding will free locked gold in a furnace calcine, due probably to the near atomic size of the gold particles.

## APPENDIX

### I Calculation of Heat Flow From Oxidizing Sulphide Particles

The following assumptions were held constant throughout this report:

An average particle diameter of .0073 cm, (200 mesh, Tyler Screen Series).

An area to diameter ratio of 10.

A temperature of 450 C for the atmosphere and surrounds of the oxidizing particles.

An emissivity of one for all radiation calculations.

A specific gravity of 4.6 for the iron sulphide.

A composition of FeS, molecular weight = 87.8, for the sulphide.

#### (A) Heat Flow by Radiation

The heat flow from the roasting sulphide particles was calculated by the Stefan-Boltzmann formula:

$$Q_r = 5.76E \left\{ \left( \frac{T_2}{1000} \right)^4 - \left( \frac{T_1}{1000} \right)^4 \right\} \text{ watts per sq cm}$$

where:  $T_2$  and  $T_1$  are the temperatures of the surface and the surroundings in degrees Kelvin and  $E$  is a fraction, the emissivity, which depends on the radiation body and which approaches one for rough black surfaces. When the above mentioned assumptions are substituted into this formula the heat loss by radiation is given by:

$$Q_r = 9.4 \times 10^6 \left\{ \left( \frac{T_2}{1000} \right)^4 - .274 \right\} \text{ cal per mole of FeS per sec.}$$

It is obvious that the above formula assumes the area of the particles to be constant during roasting. Although the diameter of the particles increases slightly because of the formation of porous iron oxide from the dense sulphide, in view of the other approximations this increase is not serious.

(B) Heat Flow by Convection

Heat loss by convection from spheres is given by Langmuirs<sup>15</sup> equation:

$$Q_c = S (\phi_2 - \phi_1) \text{ watts per sphere.}$$

where:

S includes the space factor and the thickness of the air film around each sphere.

$\phi_1$  is the thermal conduction of air at  $t_1$ , the bulk air temperature.

$\phi_2$  is the thermal conduction of air at  $t_2$ , the interface particle temperature.

For spheres, S is given by:

$$S = \frac{\pi}{2} \frac{a^2}{B} \left( 1 + \frac{4B}{a} + \sqrt{1 + \frac{8B}{a}} \right) \text{ cm}$$

where:

a is the sphere diameter.

B is the thickness of the air film around each sphere.

For still air at atmospheric pressure, experiments have shown B to equal 0.41 cm at 20 C, to be independent of the sphere temperature, and to be inversely proportional to the air density. For a bulk air temperature of 450 C, B therefore equals 1.0 cm. To ensure that the calculated convection losses were not low, B was reduced to 0.1 cm.

Langmuirs' thermal conduction factors ( $\phi$ ) for still air are as follows:

<u>Temperature</u>	<u><math>\phi</math></u>
450 C	0.20 watts per cm
500 C	0.23 watts per cm
700 C	0.36 watts per cm
1000 C	0.55 watts per cm
1500 C	1.00 watts per cm
2000 C	1.60 watts per cm

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15 Langmuir, M., loc. cit.

From the previously listed assumptions, S equals 0.0555 cm and the heat flow by convection is given by:

$$Q_c = (0.123 \times 10^7) (\phi_2 - 0.20) \text{ cal per mole of FeS per sec}$$

## II Calculation of Sulphide Oxidation Rates.

### (A) Oxidation Rate When Limited By Rate Of Oxygen Diffusion

According to the classical kinetic theory of gases the diffusion of component A in a gaseous mixture of A and B results from a driving force equal to the partial pressure gradient -  $\frac{d P_A}{d L}$  which exists in the direction of diffusion. This driving force is used to overcome a resistance to diffusion proportional to the product of the concentration of the gases. Mathematically:

$$-\frac{d P_A}{d L} = \infty_{AB} C_A C_B (V_A - V_B) \quad (1)$$

where:

$P_A$  = partial pressure of A.

$L$  = distance in the direction of diffusion of A.

$\infty_{AB}$  = a proportionality factor.

$C_A, C_B$  = molal concentrations of A and B, respectively.

$V_A, V_B$  = linear velocities of diffusion of A and B in the direction of diffusion of A.

For the roasting of iron sulphide:



there exists counter diffusion of oxygen and sulphur dioxide through an inert nitrogen gas film. Gilliland<sup>16</sup> has developed a rigorous treatment of the simultaneous diffusion of two gases in the presence of a stagnant gas film which leads to complex equations for even this relatively simple case. However, useful approximations are obtained by simple relationships based on the following assumption. In a complex system of diffusing gases, the diffusional gradient for any component A is equal to the sum of the gradients

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16 Gilliland, E.R., loc. cit.

which result from the separate diffusion of A with each of the other components in separate binary systems in which the concentrations and rate are the same as for the complex system. Thus for the diffusion of oxygen to the sulphide interface, equation (1) develops into

$$-\frac{d P_{O_2}}{d L} = \alpha_{O_2 SO_2} C_{O_2} C_{SO_2} (V_{O_2} - V_{SO_2}) + \alpha_{O_2 N_2} C_{O_2} C_{N_2} V_{O_2} \quad (2)$$

Assuming the ideal gas law to hold, the coefficient of diffusion

$D_{AB}$  of components A and B is defined as:

$$D_{AB} = \frac{(RT)^2}{\alpha_{AB} \pi}$$

where:

$\pi$  is the total pressure in atmospheres.

T = temperature, degrees Kelvin.

and:

$$V_A = r_A U_A = \frac{r_A RT}{P_A}$$

where:

$r_A$  = the molal rate of diffusion of A in moles per unit time  
per unit of cross - sectional area of diffusional path.

$U_A$  = molal volume of component A.

Making these substitutions, equation (2) yields:

$$-\frac{\pi}{RT} \frac{d P_{O_2}}{d L} = \frac{1}{D_{O_2 SO_2}} (r_{O_2} P_{SO_2} - r_{SO_2} P_{O_2}) + \frac{1}{D_{O_2 N_2}} (r_{O_2} P_{N_2}) \quad (3)$$

Because of the uncertainty of the proportionality factors,  $\alpha$ ,

and the corresponding diffusivities in mixtures of several components, an average diffusivity  $D_{Am}$  is used to replace the separate values in equation (3). The average value of the diffusion coefficient taken as the weighted mean for each pair is given by:

$$(1 - N_A) D_{Am} = N_B D_{AB} + N_C D_{AC} + \dots \quad (4)$$

where:

$N_A, N_B, \dots$  are the average mole fractions of components, A, B,  $\dots$   
in the diffusional film.

From the stoichiometry of the roasting reaction, equation A:

$$r_{SO_2} = -\frac{4}{7} r_{O_2} \quad (5)$$

$$\text{and } r_{N_2} = 0$$

Substituting equations (4) and (5) into (3) yields:

$$-\frac{\pi}{RT} \frac{d P_{O_2}}{d L} = \frac{1}{D_{O_2m}} r_{O_2} \left( P_{SO_2} + P_{N_2} + \frac{4}{7} P_{O_2} \right) \quad (6)$$

$$\text{or, since } \pi = P_{O_2} + P_{SO_2} + P_{N_2}$$

$$r_{O_2} d L = -\frac{D_{O_2m}}{RT} \pi \frac{d P_{O_2}}{\left( \pi - \frac{3}{7} P_{O_2} \right)} \quad (7)$$

Integrating between the film boundaries, L and Li, corresponding to an effective film thickness  $B_G$  gives:

$$r_{O_2} = \frac{7}{3} \frac{D_{O_2m}}{RT B_G} \ln \frac{\pi - \frac{3}{7} P_{O_2i}}{\pi - \frac{3}{7} P_{O_2}} \quad (8)$$

The diffusion coefficient  $D_{AB}$  for the interdiffusion of two gases, A and B, may be estimated from the following empirical relationship developed by Gilliland:

$$D_{AB} = 0.0043 \frac{T^{3/2}}{\pi (U_A^{1/3} + U_B^{1/3})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad (9)$$

where:

$M_A$  and  $M_B$  are the molecular weights of A and B.

All other symbols are as previously listed.

Therefore at 500 C:

$$D_{O_2SO_2} = 0.506 \text{ sq cm per sec}$$

and

$$D_{O_2N_2} = 0.644 \text{ sq cm per sec}$$

The required sulphur dioxide gradient across  $B_G$  is now found by trial and error to equal 0.12 atmospheres from equations (4), (8), the rate relationship  $r_{SO_2} = -\frac{4}{7} r_{O_2}$ , and assuming the oxygen gradient across  $B_G$  to equal 0.21 atmospheres.

Noting that the diffusion coefficient varies as the  $3/2$  power of the absolute temperature, at any temperature T:

$$D_{O_{2m}} = 0.00002947 T^{3/2} \text{ sq cm per sec}$$

and

$$r_{O_2} = \sqrt{T} \frac{(0.00000336)}{B_G} \text{ moles per sq cm per sec}$$

Thus, since one mole of oxygen oxidizes 0.571 moles FeS, the oxidation rate of FeS when oxygen diffusion controlled equals:

$$r_{FeS} = \frac{\sqrt{T}}{B_G} 0.00000192 \text{ moles FeS per sq cm per sec}$$

From the initial roasting rate measurements for FeS by Diev and Karyakin<sup>17</sup> at 700 C, 0.000525 moles per mole per second, diffusion rate controlled, the effective area, A, per mole of FeS is found to equal:

$$A = \frac{.000525 B_G}{(.00000192) \sqrt{973}} = 8.76 B_G \text{ sq cm}$$

Thus the roasting rate at the start of oxidation is given by

$$r_{FeS} = \frac{\sqrt{T} (0.00000168)}{B_G} \text{ moles FeS per mole per sec}$$

Consider now the sulphide particles, assuming spheres, and let X equal the fraction of each particle oxidized at any time, r the effective initial radius of the particles and  $r_1$  the effective instantaneous radius per mole. The momentary thickness of the oxide layer equals  $r - r_1 = r (1 - \sqrt[3]{1 - X})$  cm per mole and the momentary area of the particles =  $4\pi r^2 (1 - X)^{2/3}$  sq cm per mole. When  $B_G$  is assumed equal to 0.1 cm, as during the convection heat flow calculations, the above measured roasting rate gives an effective initial radius per mole:

$$r = 0.264 \text{ cm}$$

With these values the instantaneous oxidation rate of FeS when diffusion controlled is given by:

$$r_{FeS} = \frac{\sqrt{T} (0.00000168) 4\pi (.264)^2 (1-X)^{2/3}}{(.876)(0.1 + .264 - .264 \sqrt[3]{1-X})} \text{ moles per mole per sec}$$

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<sup>17</sup> Diev, N.P., and Karyakin, Yu.V., loc. cit.

and simplifying:

$$r_{\text{FeS}} = \frac{6.38 \times 10^{-6} \sqrt{T} (1-X)^{2/3}}{1.379 - (1-X)^{1/3}} \text{ moles per mole per sec} \quad (10)$$

This roasting rate is shown plotted against temperature for different values of X in Graph VIII.

For all values of X, the energy of activation for this diffusion, found by plotting  $\ln r_{\text{FeS}}$  VS  $\frac{1}{T}$ , is approximately 1000 cal per gram mole of FeS. While this value is considerably lower than the 3000 to 5000 cal per mole usually found for diffusion controlled reactions it nevertheless is of the right order and equation (10) may be considered to give the rate of the reaction with reasonable accuracy.

By using the spherical analogy of Ficks Second Law:

$$\frac{dC}{dt} = D \left( \frac{d^2C}{dx^2} + \frac{2}{x} \frac{dC}{dx} \right)$$

an expression for the rate of oxygen diffusion to the iron sulphide interface may be derived:

$$\frac{dm}{dt} = \frac{D 4\pi r S R}{R - r}$$

where:

m = weight of oxygen absorbed.

r = instantaneous radius of the sulphide particle.

R = original radius of the sulphide particle.

D = diffusion coefficient.

S = concentration of oxygen in atmospheres.

t = time.

This expression, however, does not check measured reaction rates and is independent of temperature and thus yields an activation energy of zero. For these reasons it is not considered further in this report.

#### (B) Oxidation Rate when Chemical Rate Controlled.

The use of the Arrhenius equation,  $K = A e^{-E/RT}$ , is too well



known to require further explanation at this point and will therefore not be considered further, except to state that A is assumed to vary as the square root of the absolute temperature.

### III Calculation Of The Oxidation Potentials For The Aqueous Media Oxidation.

The free energy, experimental, and solubility data for the aqueous media oxidation are as follows:

#### 1. Free energy data:<sup>18</sup>

- i  $\text{FeS(s)}; \Delta F_{25\text{ C}}^{\circ} = -22,900 \text{ cal per mole.}$
- ii  $\text{OH}^{-}(\text{L}); \Delta F_{25\text{ C}}^{\circ} = -37,470 \text{ cal per mole.}$
- iii  $\text{Fe(OH)}_3; \Delta F_{25\text{ C}}^{\circ} = -164,030 \text{ cal per mole.}$
- iv  $\text{SO}_4^{\equiv}; \Delta F_{25\text{ C}}^{\circ} = -176,100 \text{ cal per mole.}$
- v  $\text{Fe}^{+++}; \Delta F_{25\text{ C}}^{\circ} = -2,530 \text{ cal per mole.}$

#### 2. Experimental results:

- i Average normality of alkali medium = 4 N NaOH.
- ii Final concentration of  $\text{Fe}^{+++}$  and  $\text{SO}_4^{\equiv} = 4.13 \text{ N.}$
- iii Oxygen partial pressure = 115 psi = 7.83 atmospheres.

#### 3. Solubility data:<sup>19</sup>

- i Oxygen solubility in water at 14.7 psi and 25 C = 28.22 ml per litre.
- ii Oxygen solubility in 0.5 N NaOH at 14.7 psi and 25 C = 22.9 ml per litre.
- iii Oxygen solubility in 2.0 N NaOH at 14.7 psi and 25 C = 12.2 ml per litre.
- iv The solubility of slightly soluble gases in aqueous salt solutions

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<sup>18</sup> Lewis, G., and Randell, M., Thermodynamics and The Free Energy of Chemical Substances, McGraw-Hill Book Company, New York, 1923.

<sup>19</sup> Markhan, A., and Kobe, K., The Solubility of Gases in Liquids, Chemical Reviews, 28, 1941.

is given by:

$$S = S_0 \left( A m + \frac{1}{1 + B m} \right)$$

where:

$m$  = molarity of the salt.

$S$  = gas solubility.

$S_0$  = gas solubility in pure water.

$A, B$ , are arbitrary constants.

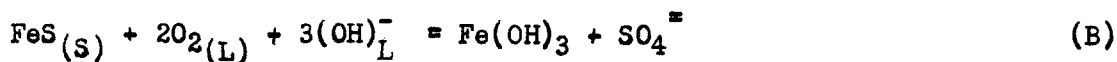
On solving,  $A = -0.078$ ,  $B = 0.356$ , and at 14.7 psi, 25 C, and in 4 N NaOH,  $S = 2.82$  ml per litre.

v When a slightly soluble gas does not form a chemical compound with the solvent, Henry's Law is obeyed within the limits allowed in engineering calculations. Thus the solubility of oxygen at 115 psi and 25 C in water = 220. ml per litre =  $9.6 \times 10^{-3}$  moles per litre.

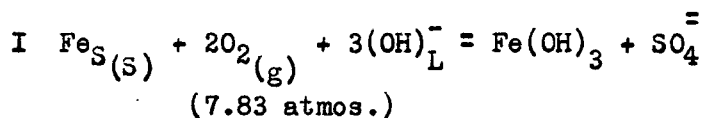
Similarly the solubility of oxygen at 115 psi and 25 C in 4 N NaOH = 22. ml per litre =  $1.0 \times 10^{-3}$  moles per litre.

#### (A) Oxidation In The Alkali Medium.

The oxidation reaction in the alkali medium is given by the equation:



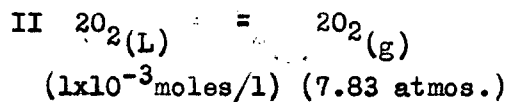
This equation may be considered in two steps:



$$\Delta F_{25C} = \Delta F^0 + RT \ln \frac{[\text{SO}_4^{=2}]}{[\text{OH}]^3 [\text{O}_2]^2}$$

$$\Delta F_{25C} = -204,820 - 4,050$$

$$\Delta F_{25C} = -208,870 \text{ cal per mole FeS}$$



$$\Delta F^0 = -RT \ln \frac{[\text{O}_{2(g)}]^2}{[\text{O}_{2(L)}]^2}$$

$$\Delta F^0 = -10,560 \text{ cal}$$

Therefore the free energy change for equation (B) = - 219,430 cal per mole FeS

Hence The oxidation potential:

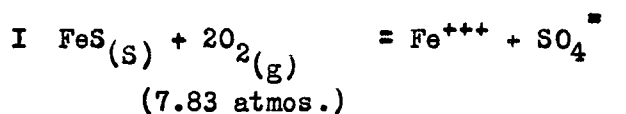
$$E_{25C} = -\frac{\Delta F}{nF} = 1.2 \text{ volts}$$

(B) Oxidation In The Neutral Medium.

The oxidation reaction in the neutral medium is given by the equation:



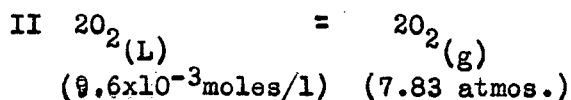
As before this equation may be split into two steps:



$$\Delta F_{25C} = \Delta F^0 + RT \ln \frac{[\text{Fe}^{+++}][\text{SO}_4^{=}]}{[\text{PO}_2]_{(g)}^2}$$

$$\Delta F_{25C} = - 155,730 - 753$$

$$\Delta F_{25C} = - 156,480 \text{ cal per mole FeS}$$



$$\Delta F^0 = -RT \ln \frac{[\text{O}_{2(g)}]^2}{[\text{O}_{2(L)}]^2}$$

$$\Delta F^0 = - 7900 \text{ cal}$$

Therefore the free energy change for equation (C) = -164,000 cal per mole FeS.

Hence the oxidation potential:

$$E_{25C} = -\frac{\Delta F}{nF} = 0.9 \text{ volts.}$$

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