STATE OF MONTANA Tim Babcock, Governor

BULLETIN 51

BUREAU OF MINES AND GEOLOGY E. G. Koch, Director

March 1966

THE RECOVERY OF ELEMENTAL SULFUR FROM SULFIDE ORES

by

Fathi Habashi Department of Metallurgy Montana College of Mineral Science and Technology

			po.
			т.
			J
			ÿ
			w.

STATE OF MONTANA BUREAU OF MINES AND GEOLOGY E. G. Koch, Director

BULLETIN 51

THE RECOVERY OF ELEMENTAL SULFUR

FROM SULFIDE ORES

bу

Fathi Habashi
Department of Metallurgy
Montana College of Mineral Science and Technology



MONTANA COLLEGE OF MINERAL SCIENCE AND TECHNOLOGY Butte, Montana March 1966

Price \$1.50

Montana Bureau of Mines and Geology

Room 203-B, Main Hall

Montana College of Mineral Science and Technology

Butte, Montana

C O N T E N T S

Abstrac	t	age iv
Introdu	ction	1
Pyromet	allurigical methods	2
rne	rmal dissociation	2
Pro	duction of culturation SO	2
Pod:	duction of sulfur via SO ₂	3 5
Ch1	uction smelting	5
Hudnomo	orination of sulfide ores	9
Dno.	tallurgical methods	15
Λαυ	duction of sulfur via H ₂ S	15 16
Floatno	eous oxidation of sulfide ores	
Fle	lytic methods	17 17
Fle	ctrolysis of sulfide anodes in aqueous phase	19
Literati		25
LICCIAC	ure	45
	ILLUSTRATIONS	
Figure		
1.	Recovery of elemental sulfur from pyrite by reaction	
	with SO_2 gas	3 6
2.	Reduction of SO ₂ to elemental sulfur by natural gas.	6
3.	Recovery of elemental sulfur and copper from pyrite	
	by reduction smelting	7
4.	Modified Malm process	11
5.	Recovery of elemental sulfur from pyrite by	
. 9.1	chlorination	12
6.	Recovery of elemental sulfur, tin, and zinc from	
	pyrite ore	14
7.	pyrite ore	
_	formation	16
8.	Recovery of nickel and elemental sulfur by	
	electrolysis of nickel sulfide anodes	23
9.	The International Nickel Company Thompson Refinery,	
	Manitoba, Canada	24
10.	Nickel sulfide electrolytic plant, Thompson Refinery	24
	TABLES	
Table		
7	The Only I a made age	0

ABSTRACT

Pyrometallurgical, hydrometallurgical, and electrolytic processes aimed to recover the metals from their sulfide ores and at the same time the by-product sulfur in the elemental form, are reviewed. Pyrometallurgical methods involve thermal dissociation, reaction of sulfide ores with SO₂ gas, production of sulfur via SO₂, reduction smelting, and chlorination. Hydrometallurgical methods involve the production of sulfur via H₂S, and the aqueous oxidation of sulfide ores. Electrolytic methods involve electrolysis of molten sulfides, and the electrolysis of sulfide anodes in aqueous phase.

THE RECOVERY OF ELEMENTAL SULFUR FROM SULFIDE ORES

by Fathi Habashi

INTRODUCTION

During the smelting of copper, nickel, lead, and zinc sulfide ores, large amounts of sulfur dioxide are produced. Because the release of this gas in the atmosphere causes pollution problems, many attempts were made in the past for its recovery. In one example, pure SO₂ was obtained from flue gases by an absorption-desorption process, and in another example, the smelting operation was conducted with oxygen instead of air, to get a relatively concentrated SO₂. In both cases SO₂ recovered was either liquified or processed to sulfuric acid. Although these two forms of sulfur are the usual forms that are consumed by the chemical and metallurgical industries, yet their storage and transport usually raise economic problems. Unless they are used in the smelter itself, or a market exists near the smelter, the process will be uneconomical.

It was realized, long ago, that a process by which sulfur can be recovered directly in the elemental form would be most attractive. This applies not only to the processing of nonferrous metals but also for pyrite or pyrrhotite ores whose shipping costs to sulfuric acid manufacturers may be, in some cases, prohibitive. Elemental sulfur is easily stored and transported, weighs only one half an equivalent quantity of SO₂ and one third as much as the corresponding quantity of sulfuric acid, and is readily converted to any of these forms when needed.

In this paper, an attempt will be made to review all the processes that are aimed to recover the metals from their sulfide ores, and at the same time the by-product sulfur in the elemental form.

PYROMETALLURGICAL METHODS

1. Thermal Dissociation

To reduce the shipping costs of pyrite, the Noranda Company in Canada has designed a plant in which pyrite is first heated in absence of air to distill off one atom of sulfur in the elemental form, then roasting the residue to SO_2 for sulfuric acid manufacture (i.e.)

$$FeS_{2} \longrightarrow FeS + S \dots \dots (1)$$
2 FeS +7/2 $O_{2} \longrightarrow Fe_{2}O_{3} + 2 SO_{2} \dots (2)$

2. Reaction of Sulfide Ores with SO2

An improvement in the thermal dissociation method is to utilize sulfur dioxide in distilling off elemental sulfur from pyrite or pyrrhotite at 800-900°C according to:

3
$$\operatorname{FeS}_2 + 2 \operatorname{SO}_2 \longrightarrow \operatorname{Fe}_3 \operatorname{O}_4 + 8 \operatorname{S} \cdot \cdot \cdot (3)$$

3 $\operatorname{FeS} + 2 \operatorname{SO}_2 \longrightarrow \operatorname{Fe}_3 \operatorname{O}_4 + 5 \operatorname{S} \cdot \cdot \cdot (4)$

Sulfur dioxide for the reaction can be produced by burning some of the pyrite with air. The process was developed by the Duisburger Kupferhutte in Germany (Schackmann, 1954). Under these conditions, non-ferrous metals present in the pyrite are transformed into sulfates, which can be recovered from the cinder by leaching (Fig. 1). Thermodynamic and kinetic studies of the above reactions were conducted by Wohler et al. (1923), Rosenqvist and Hyne (1953), Morawietz (1954), Schmahl (1954), Iriarte et al. (1963), and Pannetier and Davignon (1963).

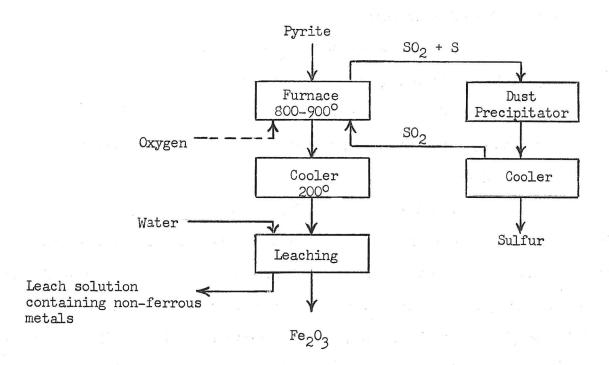


Fig. 1 - Recovery of Elemental Sulfur from Pyrite by Reaction with SO Gas. The Duisburger Kupferhutte Process.

3. Production of Sulfur via SO₂

Sulfur dioxide can be reduced to elemental sulfur by coke, methane, or natural gas at about 1200°C.

a) Reduction by coke

The reaction

$$SO_2 + C \longrightarrow CO_2 + S \dots (5)$$

is exothermic. However, the conditions are favorable for the reaction:

$$CO_2 + C \longrightarrow 2 CO \dots (6)$$

to take place, which is endothermic. To achieve the required temperature in the reduction, exaternal heating must be supplied, and the simplest

method is by introducing oxygen to utilize the exothermic combustion of carbon.

Carbon monoxide formed according to equation (6) reacts with $\rm SO_2$ at $600^{\circ}\mathrm{C}$ to form elemental sulfur:

$$SO_2 + 2 CO \longrightarrow 2 CO_2 + S \dots (7)$$

Carbon oxysulfide is formed by a side reaction:

However, it can be converted to elemental sulfur easily when passed over bauxite at 425-450°C:

$$2 \cos + so_2 \longrightarrow 2 \cos_2 + 3 s \dots (9)$$

Coke consumption, which is the major factor in the process, is about 0.4 tons/ton sulfur. The thermodynamics and kinetics of this process were discussed by Lepsoe (1938, 1940). The process was operated by the Consolidated Mining and Smelting Company in Trail, Canada, and was described by King (1950). The plant was shut down in 1943 because SO₂ was needed for making H₂SO₄ locally to meet the fertilizer demand. Before the shut down, the production was 150 tons/day of sulfur of 99.99% purity.

b) Reduction by methane and natural gas:

Sulfur dioxide is reduced by methane at 1250°C to elemental sulfur according to:

$$2 SO_2 + CH_4 \longrightarrow CO_2 + 2 H_2O + 2 S . . (10)$$

Reduction with methane was tried by Young (1915), and later natural gas was used by Fleming and Fitt (1942) on a pilot scale (5 tons/day sulfur) in the 1940's for $4\frac{1}{2}$ years at the American Smelting and Refining Company in Garfield, Utah. The gas contained 5.5-7.25% SO₂ and the sulfur produced was 99.9% pure. A plant description was given by Fleming and Fitt (1950).

The combustion takes place in a large vertical steel chamber lined with refractory and insulating bricks. In order to obtain surface for complete combustion, the chamber is packed with a checker work of refractory brick.

Small amounts of hydrogen sulfide and carbon oxysulfide are formed by side reactions:

$$SO_2 + CH_4 \longrightarrow H_S + CO + H_2O \dots (11)$$
 $CO + S \longrightarrow COS \dots (8)$

Both can be converted to elemental sulfur by passing the gas mixture over a suitable catalyst at the right temperature. Carbon oxysulfide reacts according to equation (9), and hydrogen sulfide reacts at 210-235°C in contact with activated alumina, according to:

$$2 \text{ H}_2 \text{ S} + \text{SO}_2 \longrightarrow 2 \text{ H}_2 \text{ O} + 3 \text{ S} \dots \dots (12)$$

Sulfur is formed in the gases as a mist and is collected in electrostatic precipitators. A flowsheet is shown in Fig. 2. The process is simple and efficient; it was shut down only because of shortage in the supply of natural gas.

4. Reduction Smelting

Elemental sulfur was first successfully recovered as a by-product from the blast-furnace smelting of pyritic copper ore by Orkla Grube Aktiebolag at a small plant at Lokken, Norway in 1928. The success of this pilot plant led to the construction in 1932 of a large modern smelter with four blast furnaces. Similar operations are in Ronnskar (Sweden), Mina de S. Domingos (Portugal), Rio Tinto (Spain), and USSR.

This method is only economical for pyrites containing copper. The ore is mixed with coke, quartz, and limestone and heated in a blast furnace (Fig. 3). Copper is recovered as a molten matte, and iron is eliminated

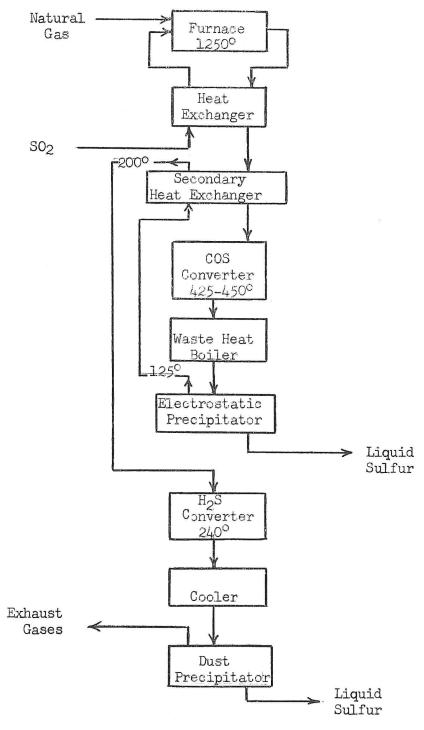


Fig. 2 - Reduction of SO_2 to Elemental Sulfur by Natural Gas.

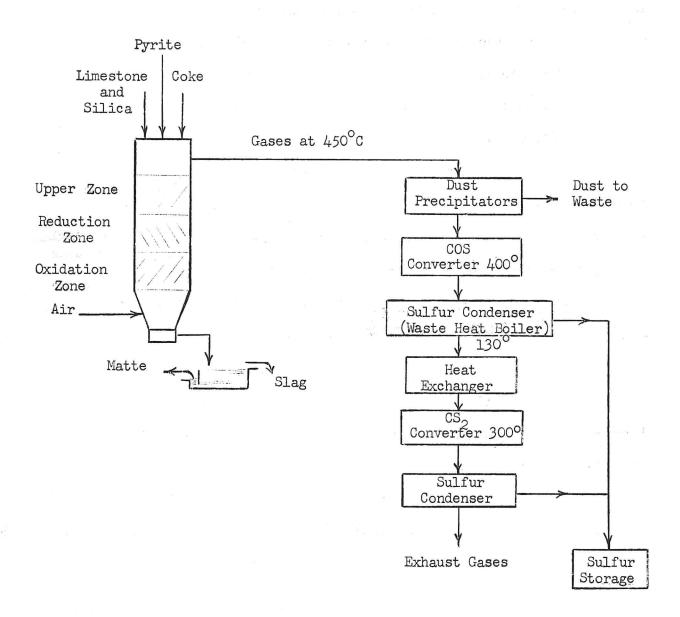


Fig. 3 - Recovery of Elemental Sulfur and Copper from Pyrite by Reduction Smelting (The Orkla Process).

in the slag. In the upper part of the furnace, one atom of sulfur in pyrite is distilled as elemental sulfur. In the oxidizing zone, FeS formed is oxidized to ferrous oxide and SO_2 . In the middle part of the furnace, the reduction zone, SO_2 is reduced by coke to elemental sulfur which is volatilised as vapor. The reactions taking place can be represented by the following equations:

Upper zone:
$$FeS_2 \longrightarrow FeS + S....(13)$$

Oxidation zone: $FeS + O_2 \longrightarrow FeO + SO_2....(14)$

Middle zone: $SO_2 + C \longrightarrow CO_2 + S.....(15)$

The method has the disadvantage that only copper is recovered; from and other metals present in pyrite, e.g. cobalt and zinc, are not recovered.

The matte produced contains 6-8% Cu, is unsuitable for direct converting, and is usually re-smelted with coke, silica, and limestone to 40% Cu.

Carbon disulfide and carbon oxysulfide are formed in the furnace; they are, however, converted to elemental sulfur on catalytic beds;

$$CS_2 + SO_2 \longrightarrow CO_2 + 3 S \dots \dots \dots (16)$$

$$2 COS + SO_2 \longrightarrow 2 CO_2 + 3 S \dots \dots \dots (17)$$

Table 1 gives average analysis of the ore treated in Norway, and the composition of slag, matte, and the exit gases from the furnace.

Table 1 - The Orkla Process (after Kiaer, 1954)

Analysis of ore	_Slag	g and mat	te_	Exit g	ases from	furnace
%		Slag %	Matte %		% Vol.	g/M^3
S 41.0 Cu 1.8-2.5 Fe 38.0 Zn 1.9	Cu Fe S SiO ₂	0.3 42.0 2.3 33.5	38.50 32.46 25.55 0.14	S CO CO ² O ₂	13.2 0.2 0.5	300
Co 0.1 SiO ₂ 12-16 Al ₂ O ₃ 0.3 CaO 0.8	Zn ~ CaO Al ₂ O ₃ MgO	1.6 4.5 1.4 0.13		\$0 ₂ #25 CS ₂ CO ₂		75.0 12.3 28.8 22.3
As 0.05 Se 0.005 Ag 20.0 g/ton Au 0.2 g/ton	Co		0.11			

Ores containing arsenic, as is the case in Rio Tinto, are difficult to treat. Sulfur vapor containing a large percentage of arsenic starts to condense at 350°C, but arsenic-free vapor condenses at a much lower temperature. Further, liquid sulfur containing arsenic is very viscous and therefore is difficult to handle. Owing to these facts, passing the gases over catalyst beds for converting CS₂ and COS to S is not successful.

5. Chlorination of Sulfide Ores

Chlorine reacts with metal sulfides readily to form metal chlorides and elemental sulfur:

$$MS + Cl_2 \longrightarrow MCl_2 + S \dots (18)$$

The use of chlorine for the treatment of sulfide ores is an old technique, and much work was published in this connection. However, no plants are at present operating, although the process is very promising. The reaction can be conducted in two ways:

- a) Low-temperature chlorination at 60-100°C, i.e., at temperature below the melting point of sulfur so that the liberated sulfur does not melt and agglomerate the charge. In the past, seemingly no attempts were made to recover the sulfur.
- b) High-temperature chlorination at 400-700°C. In this process sulfur is volatilized, condensed, and recovered.

The chlorination reaction is strongly exothermic, and therefore, once started, it would require no external heat. The required reaction temperature can be controlled simply by adjusting the flow of chlorine to the reactor. In both processes, the non-ferrous metals are converted to chlorides and are recovered usually by leaching. The leach solution is first purified

from iron by adding zinc oxide to precipitate ferric hydroxide. Each metal is then separated by successive cementation, and good and silver by copper, copper by lead, and lead by zinc. The final solution, containing only zinc, is evaporated under recount to anhydrous zinc chloride, which is then electrolyzed in the fused state to metal and chlorine. Molten zinc cathode and graphite anode are used. The chlorine is collected and reused for the process.

Practically all sulfide cres contain pyrite, which is also easily chlorinated, but there is no chlorine lost in the process, as FeCl₂ formed is readily decomposed by oxygen liberating chlorine as follows:

$$2 \text{ FeCl}_2 + 3/2 \circ_2 \longrightarrow \text{Fe}_2 \circ_3 + 2 \circ \circ_2 \dots \dots (19)$$

Also, if any FeCl₃ is formed, it itself acts as a chlorinating agent for the other sulfides in the ore:

$$CuS + 2 FeCl_3 \longrightarrow 2 FeCl_2 + CuCl_2 + S . . (20)$$

NiS + 2 FeCl₃
$$\longrightarrow$$
 2 FeCl₂ + NiCl₂ + S . . (21)

It also reacts with pyrite according to the equation:

$$FeS_2 + 2 FeCl_3 \longrightarrow 3 FeCl_2 + 2 S \dots (22)$$

Historically, the high-temperature chlorination process was developed first. Thus, as early as 1897 Ashcroft patented this process, and a plant was operated at Broken Hill, Australia, for the treatment of a lead-zinc ore.

In USA, John L. Malm of The Western Metal Company developed the low-temperature chlorination process, and a 10 t/day plant was in operation in Corbin, Montana, and another 50 t/day plant at Georgetown, Colorado. The Bunker Hill & Sullivan Mining and Concentrating Co. planned a plant at Kellogg, Idaho, but the idea was not fulfilled, seemingly because of financial difficulties. The process is known as the Malm process and was described by Traphagen (1909) and Herrick (1910).

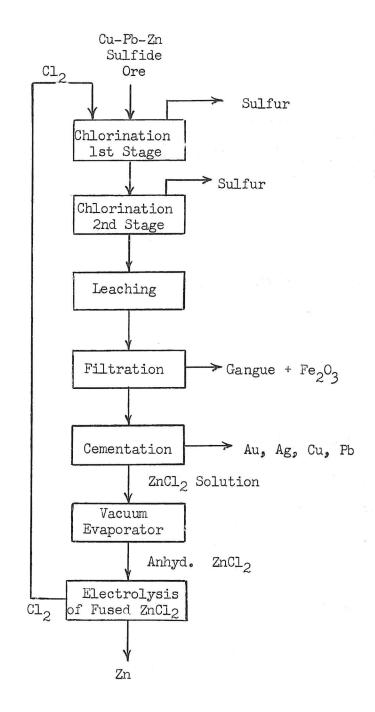


Fig. 4 - A Modified Malm process.

(Ionides, 1916).

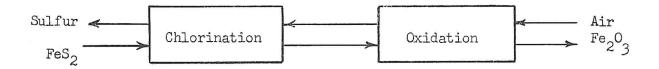


Fig. 5 - Recovery of Elemental Sulfur from Pyrite by Chlorination (Comstock-Wescott Process).

Ionides (1916) described a modified Malm Process, which was operated by the Midwest Metals Co. Chlorination was conducted in two stages—in the first stage by chlorine gas, and in the second by simple roasting so that any FeCl₃ formed in the first stage reacts with the non-ferrous metal sulfides. Fig. 4 shows a flowsheet of the process. Ores treated by this process had the following analysis:

Pb	9.0%	
Zn	2.5%	
Cu	0.5%	
Ag	3.0	Oz/t
Au	0.05	0z/t

The high-temperature process was applied to pyrite containing small amounts of lead and zinc (Levy and Gray, 1928). Later, the same process was applied to pyrite for the sole purpose of the recovery of elemental sulfur. Thus, in 1936 a plant was operated in Canada by the Comstock-Wescott Inc.,

Niagara Falls, in which pyrite was treated with chlorine gas in rotary kilns to volatilize elemental sulfur according to:

$$2 \text{ FeS}_2 + 2 \text{ Cl}_2 \longrightarrow 2 \text{ FeCl}_2 + 4 \text{ S. (23)}$$

Ferrous chloride was oxidized by air to generate the chlorine for recycle:

$$2 \text{ FeCl}_2 + 3/2 \text{ O}_2 \longrightarrow \text{Fe}_2 \text{O}_3 + 2 \text{ Cl}_2 \dots (24)$$

The plant was described by Rowe (1938) and the process is covered by numerous patents. Fig. 5 shows a flowsheet of the process.

The high-temperature process was studied further by Zielinsky (1931), Urazov et al. (1935), Pristoupil (1937), Ezdakov (1939), Chowdhury and Hossain (1945), Hayek and Kraus (1950), Khundkar and Quadr (1951) and Biswas et al. (1951-55).

Recently, a pilot plant was operated by Hohn et al. (1954-58) for the treatment of pyrite containing nickel and copper. It was possible to recover sulfur in the elemental form, and the nonferrous metals were converted to chlorides and leached from the iron oxide residue. Instead of rotary kilns, fluidized beds were used. The same authors also treated an ore containing 85.6% FeS₂, 2.7% cassiterite, 6.3% zinc blende, and 5.4% gangue, and were able to get two separate fractions: 1) pigment grade Fe₂O₃ and 2) SnO₂ and ZnCl₂ fraction, which after leaching the zinc analyzed 63.8% gangue, 33.2% SnO₂, and 2.9% Fe₂O₃. This was achieved by admitting only the required amount of ferric chloride vapor to expel the sulfur from the ore, and the rest of the ferric chloride was oxidized in a separate chamber to recover chlorine and pigment grade ferric oxide:

$$2 \text{ FeCl}_3 + 3/2 \, 0_2 \longrightarrow \text{Fe}_2 \, 0_3 + 3 \, \text{Cl}_2 \dots (25)$$

Chlorine is then allowed to react with ferrous chloride in a third chamber to volatilize pure FeCl₂:

$$\operatorname{FeCl}_2 + \frac{1}{2} \operatorname{Cl}_2 \longrightarrow \operatorname{FeCl}_3 \ldots \ldots (26)$$

Under these conditions, cassiterite is not chlorinated, and therefore can be concentrated in a separate fraction. Fig. 6 shows a flowsheet of the process.

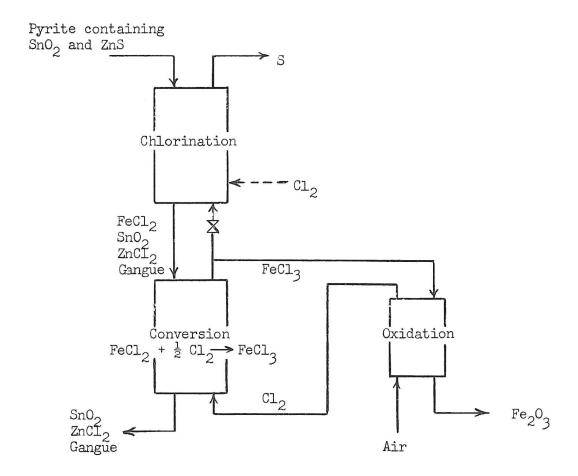


Fig. 6 - Recovery of Elemental Sulfur, Tin, and Zinc from Pyrite Ore (Hohn et al. 1957).

The US Bureau of Mines is showing interest in these processes, and work was conducted along similar lines by Kershner (1961), Donaldson (1962), and Starliper and Kenworthy (1964).

HYDROMETALLURGICAL METHODS

l. Production of Sulfur via H2S:

Pyrrhotite or ferrous sulfide produced by the thermal dissociation of pyrite, reacts readily with dilute acids to liberate hydrogen sulfide:

$$FeS + 2 H^{+} \longrightarrow Fe^{2+} + H_{2}S \dots (27)$$

The gas is collected and oxidized in a Claus furnace to elemental sulfur according to:

$$H_2S + \frac{1}{2}O_2 \longrightarrow S + H_2O \dots (28)$$

During the decomposition of FeS with acid, the non-ferrous metal sulfides are not dissolved, and therefore can be recovered from the unreacted residue. Fig. 7 shows a flowsheet of the process.

Lindenlaub (1954) treated a zinc blende concentrate:

with 60% H₂SO₄ at 150-160°C. Reaction gas containing 30-40% H₂S was passed through a Claus kiln. The residue, after washing and filtration, contained all the lead, silver, and gold, and was processed for recovery. The filtrate was treated with H₂S to precipitate copper and cadmium, which are then processed and recovered electrolytically. Spent electrolyte was concentrated and recycled.

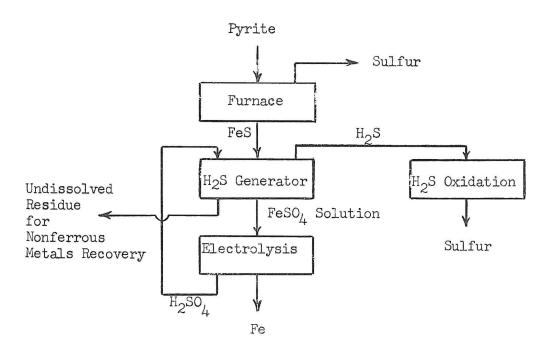


Fig. 7 - Recovery of Elemental Sulfur from Pyrite Via H2S Formation.

2. Aqueous Oxidation of Sulfide Ores:

Ferric sulfate or ferric chloride solutions dissolve metal sulfides at room temperature with the liberation of elemental sulfur:

$$ZnS + 2 Fe^{3+} \longrightarrow Zn^{2+} + 2 Fe^{2+} + S . . . (29)$$

Ferrous ion formed is oxidized by air back to ferric, thus allowing the recycle of the leaching agent. The main difficulty with this process is the hydrolysis of ferric ion and precipitation of hydrated ferric oxides, if the pH of the solution exceeds 3.5. Other oxidizing agents were suggested

to replace ferric ion. Thus chlorine water, scdium hypochlorite, nitrates, etc., were used, e.g.

$$CuS + Cl_2 (aq) \longrightarrow Cu^{2+} + S + 2 Cl^{-} \dots (30)$$

$$MoS_2 + 9 ClO^- + 6 OH^- \longrightarrow MoO_4^{2-} + 2 SO_4^{2-} + 9 Cl^- + 3 H_2O.$$
 (31)

Recently, air or oxygen under pressure was used as the oxidizing agent, at temperature below 120°C, the m.p. of sulfur. Such oxidizing agents have the advantage of not contaminating the leach solution with foreign ions, e.g.:

$$ZnS + 2 H^{+} + \frac{1}{2} O_{2} \longrightarrow Zn^{2+} + S + H_{2}O \dots \dots \dots \dots (32)$$

$$CuS + 2 H^{+} + \frac{1}{2} O_{2} \longrightarrow Cu^{2+} + S + H_{2}O \dots (33)$$

Elemental sulfur is recovered from the unleached residue by melting and filtration.

Pyrrhotite was also treated in a similar way (Downes and Bruce, 1955), but owing to the hydrolysis of ferric ion even at low pH, elemental sulfur and hydrated ferric oxide were obtained:

Nonferrous metals present in the pyrrhotite go into solution and can be recovered. Ferric oxide, which is now free from non-ferrous metals, can be readily dried, sintered, and charged to blast furnace.

ELECTROLYTIC METHODS

1. Electrolysis of Molten Sulfides

In the process for the chlorination of sulfide ores described earlier, elemental sulfur and the metal chloride were obtained; the latter was electrolyzed in the fused state to metal and chlorine, which was recycled.

In 1906, it was found by Townsend, and Valentine and Betts that the sulfide can be electrolyzed directly in the molten state to yield the metal and elemental sulfur. As most metal sulfides have either a high melting point or decompose upon melting, electrolysis is usually carried out in a metal chloride-alkali chloride bath to which the metal sulfide is added. The decomposition potential of the sulfides is usually much less than that of the chloride components of the bath, thus allowing the deposition of the metal at the cathode and elemental sulfur at the anode:

Because the solubility of most metal sulfides in metal chlorides at 700 to 800°C is usually low, electrolysis is conducted when the sulfide is either in form of suspension in the electrolyte or as a molten layer floating above the electrolyte. The deposition of the metal at the cathode, and sulfur at the anode takes place possibly by secondary reactions as follows:

$$Na^{+} + e^{-} \longrightarrow Na \dots \dots (38)$$

$$MS + 2 Na \longrightarrow M + 2 Na^{+} + S^{2-} \dots (39)$$

$$2 Cl^{-} \longrightarrow Cl_{2} + 2 e^{-} \dots (40)$$

$$S^{2-} \longrightarrow S + 2 e^{-} \dots (41)$$

Chlorine liberated at the anode does not interfere with the process, as it will react with the metal sulfide as follows:

$$MS + Cl_2 \longrightarrow MCl_2 + S \dots (42)$$

Theoretical studies on the electrolysis of sulfides were published by Truthe (1912) and Savelsberg (1940) and laboratory experiments as follows:

Sulfide	Reference
PbS	Valentine and Betts (1906) Isgaryshev and Grigor'ev (1936) Angel and Garnum (1945)
	Winterhager and Kammel (1956) Guld'in et al. (1960) Kammel (1961)
CuaS	Hoar and Ward (1958)
Cu ₂ S Sb ₂ S ₃	Vivian (1936) Kammel (1961)

Richardson (1936) described briefly a semi-commercial plant in Wales recovering lead 99.95% purity and sulfur 99.5% pure from galena by this method. The plant was operated by the National Smelting Company (1934-35), who has many patents in this connection.

2. Electrolysis of Sulfide Anodes in Aqueous Phase:

The previous method of electrolyzing sulfides in the molten state has the disadvantage of operating at temperatures in the range 500-900°. A much simpler method is to cast the sulfide in form of anodes, and electrolyze it using an aqueous electrolyte at room temperature. The process can be represented by the equations:

Anodic reaction:
$$MS \longrightarrow M^{2+} + S + 2 e^{-} \dots (43)$$

The metal deposits at the cathode, while elemental sulfur remains adhering to the anode in form of a sludge, which can be melted, separated, and recovered. This process has a great advantage over conventional methods of metal recovery. Thus, in the case of nickel extraction it would be possible to cast the nickel matte in form of anodes, and recover the metal and the sulfur directly in one step, instead of roasting the matte to oxide, reduction of the oxide to metal, and then casting the metal in form of anodes for electrolytic refining. It should also be noted that this direct electrolysis

of sulfide anodes not only by-passes the roasting and reduction step, but it is possible to recover the sulfur directly in the elemental form.

As early as 1882, Marchese patented a process based on the above idea, in which a matte having the composition: Cu 15, Pb 14, Fe 41, and S 25%, was electrolyzed. According to Engelhardt (1932) the process was applied on a commercial scale by the Scoietà Anonyma Italiana di Miniere di Rame e di Eletrometallurgia at Casarza near Genua, Italy, and by the Aktiengesellschaft für Bergbau-, Blei- und Zinkhüttenbetriebe at Stolberg, Rheinland, Germany. The process was unsuccessful, however, owing to the contamination of the electrolyte during electrolysis. Borchers et al. (1906) developed the process further by using the white metal (Cu 78.2%, S 19.6%) instead of the matte, and a pilot plant was operated by the Mansfeldschen Kupferschiefer Company at Eisleben, Germany. It appears, however, that the process never went into commercial operation. Further studies in this direction were carried out by the Russian workers Lochkarev et al. (1945), Chizhikov et al. (1948, 1956, 1963), Furtunatov and Mikhailovskaya (1951), and Klochko and Mironova (1954).

The International Nickel Company of Canada, to apply the process to nickel matte, erected a pilot plant in 1951 and full scale plant at the Thompson Refinery in Mannitoba in 1964. In this method nickel sulfide matte is melted at 980° C and cast into anodes having the dimensions $28\frac{1}{2}^{"} \times 43\frac{1}{2}^{"} \times 13^{"}$. The anodes are allowed to cool in the molds to 540° C and then promptly placed in a controlled cooling box to maintain a desired cooling rate. This step is a critical operation in preparing the anodes, otherwise the castings crack, owing to the phase transformation in Ni₃S₂ that takes place at 505° C. The analysis of anodes and electrolyte is as follows:

A	nodes	Electrolyte (pH = 4,)
Ni Cu Co Fe S	% 76.0 2.6 0.5 0.5 20.0	Ni ²⁺ g/l SO,2 100 NaCl 100 H ₃ BO ₃ 20	

Boric acid acts as a buffer to minimize variations in the pH. The anodes corrode smoothly and uniformly, and the sludge formed is granular and porous and remains adhering on the anode. The anode increases in thickness during electrolysis, owing to the formation of elemental sulfur. By the end of electrolysis the thickness is usually doubled. Also, the cell voltage rises from 3.0 volts at the start to 5.0 volts at the end of electrolysis. The temperature of electrolyte is 55-60°C. The anodes can be electrolyzed to about 10% scrap, and the efficiency during the anode dissolution is 95%. To facilitate the handling of the scrap anodes containing the sludge, they are enclosed in bags during electrolysis.

During electrolysis, Fe, Cu, Co, As, and Pb originally present in the anodes go into solution, while the precious metals are collected in the sulfur sludge. The electrolyte is regenerated by first oxidation and hydrolysis of iron, then selective oxidation with chlorine and hydrolysis of cobalt, arsenic, and lead, and finally cementation of copper by nickel powder. The nickel content of the electrolyte and the pH are adjusted and it is recycled (Fig. 8).

The sulfur sludge recovered during electrolysis, after filtration and washing to remove the electrolyte, analyzes as follows:

Elemental sulfur	97.0%
Sulfide sulfur	0.7
Nickel	1.25
Iron	0.6
Copper	0.3
Selenium	0.15
Precious metals	variable
Moisture content	20.0

The first step in the purification of the sulfur sludge (Fig. 8) involves melting and filtering. The filtrate is pure sulfur containing only 0.15% Se. The residue, analysing 50% sulfur, contains all the precious

metals and base metal values. Sulfur is purified from selenium by distillation in a 60-trays bubble cap tower, whereby a product containing 5 ppm Se is obtained at the top of the tower. At the bottom of the tower a fraction is drawn containing 20% Se. The residue containing the precious metals is melted and cast into anodes; these analyse as follows:

S	27.2%
Ni	50
Cu	20
Fe	2
Ag	0.5
Precious)	0.3
metals \int	0.3

These anodes are electrolysed in the same way as the primary nickel sulfide anodes. During electrolysis a sludge is obtained containing 90% S and 10% precious metals. This sludge is again melted and filtered to separate sulfur from the precious metals concentrate. Fig. 9 and 10 show a general view of the INCO Thompson Refinery and the electrolytic plant.

Similar work is under way at Montana College of Mineral Science and Technology in Butte, Montana, USA, in which the white metal (${\rm Cu}_2{\rm S}$) is cast in form of anodes and electrolyzed in ${\rm CuSO}_4$ solution to deposit copper at the cathode and collect sulfur at the anode.

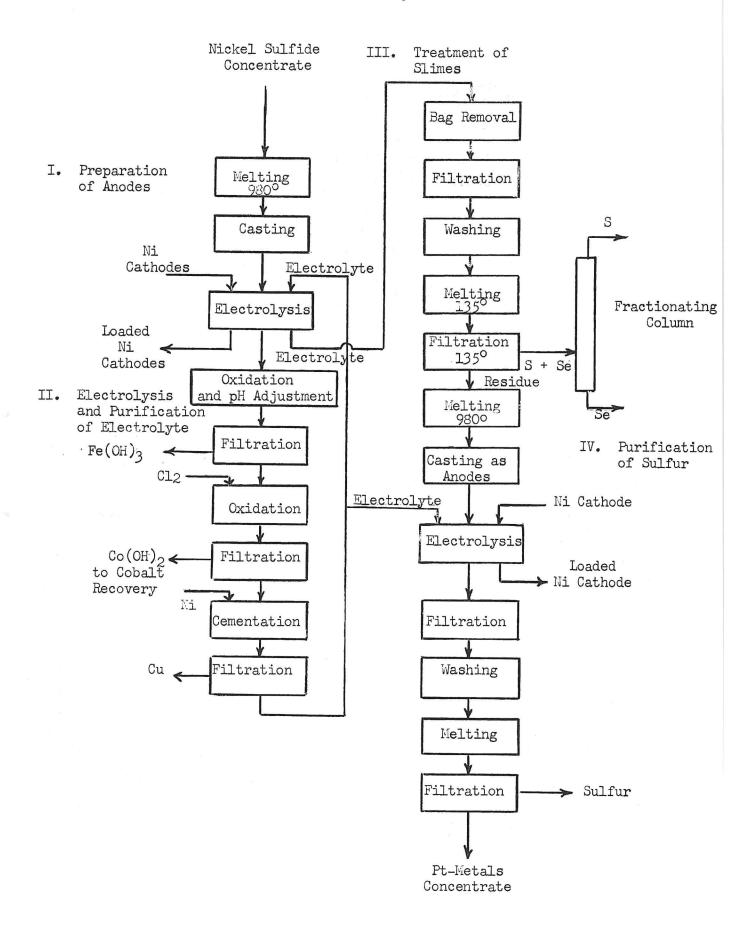


Fig. 8 Recovery of Nickel and Elemental Sulfur by Electrolysis of Nickel Sulfide Anodes (INCO Process).

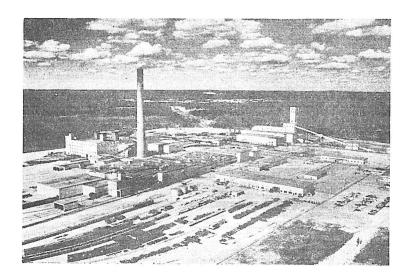


Fig. 9- The International Nickel Company Thompson Refinery, Manitoba, Canada. General View.

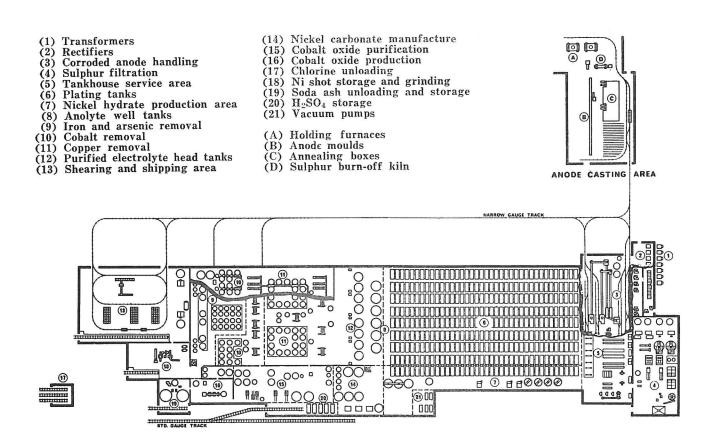


Fig. 10- Nickel Sulfide Electrolytic Plant, Thompson Refinery. (Spence and Cook 1964).

LITERATURE

INTRODUCTION

Anonymous

Hi-Purity Liquid Sulfur Dioxide from Roaster Gases Chem. Eng. 60 (4), 276-7 (1953)

Anonymous

Liquid Sulfur Dioxide Chem. Eng. 62 (10), 320-4 (1955)

M. P. Appleby

The Recovery of Sulfur from Smelter Gases
Trans. Soc. Chem. Ind. 56, 139-46T (1937). CA 31, 5955

F. Benitez

Flash Smelting Improves Harjavalta's Metallurgy Eng. Min. J. 154 (10), 76-80 (1953)

D. Bienstock, L. W. Brunn, E. M. Murphy, and H. E. Benson Sulfur Dioxide - Its Chemistry and Removal from Industrial Waste Gases US Bur. Mines Inform. Circul. 7836 (1958)

D. W. Breck and I. V. Smith
Sulfur Recovery Process Goes into Pilot Plant
Chem. Eng. 67 (25), 86-8 (1960)

P. Bryk et al. Flash Smelting Copper Concentrates J. Metals 10, 395-400 (1958)

R. S. Dean
Present Status of Sulfur Fixation and Plan of Investigation
US Bur. Mines Rept. Inves. 3339 (1937)

E. P. Fleming and T. C. Fitt Liquid Sulfur Dioxide from Waste Smelter Gases Ind. Eng. Chem. 42, 2253-8 (1950) Gmelin.

Handbuch der anorganischen Chemie. System Number 9. Schwefel, Teil A. pp. 219-23 (1953) Verlag Chemie, Weinheim. Literature reviewed to 1949.

INCO Staff

The Oxygen Flash Smelting Process of the International Nickel Company Bull. Can. Min. Met. 48, 292-300 (1955)

S. Katell and L. Fan

Bibliography of Processes for Removing Hydrogen Sulfide from Industrial Gases US Bur. Mines Inform. Circul. 7886 (1958)

M. Katz and R. J. Cole

Recovery of Sulfur Compounds from Atmospheric Contaminants Ind. Eng. Chem. 42, 2258-69 (1950)

D. A. Martin and F. E. Brantley

Selective Adsorption and Recovery of Sulfur Dioxide from Industrial Gases by Using Synthetic Zeolites
US Bur. Mines Rept. Invest. 6321 (1963)

Ontario Research Foundation

The Removal of Sulfur Gases from Smelter Fumes Ontario Dept. Mines Techn. Surveys (1949)

B. K. Shilber and M. W. Hovey

Processes for Recovering Sulfur from Secondry Source Material US Bur. Mines Inform. Circul. 8076 (1962)

P. Zurcher

Sulfur from Industrial Gases - Literature Survey Petrol. Processing 7, 333-8 (1952)

PYROMETALLURGICAL METHODS

1. Thermal Dissociation

Anonymous

Noranda's Elemental Sulfur Plant Slated to Begin Operation October 1 Eng. Min. J. 155 (9), 142 (1954)

2. Reaction of Sulfide Ores with SO2

Imperial Chemical Industries
Roasting Pyrites
French Patent 744,187 (1933) . CA 27, 3905

C. Iriarte, A. Fernandez-Olazabal, and A. Vian
Kinetics of the Reaction Between Sulfur Dioxide and Synthetic-Pyrrhotite
Proceeding from the Desulfurization of Commercial Pyrite Ores
Anales Real Soc. Espan. Fis. Quim. (Madrid), 59, 389-400, 585-94 (1963)

W. Morawietz
Thermal Oxidation of FeS, with SO, to Elementary Sulfur Z. Elektrochem. 57, 539-48 (1953). CA 68, 3115i

G. Pannetier and L. Davignon
Action of SO on Iron Sulfides
Comp. Rend. 256, 4447-9 (1963). CA 59, 3523g

G. Pannetier and L. Davignon

Etude Chimique et Cinétique de l'Action de L'Anhydride Sulfureux sur le Fer et ses Composés Sulfures

Bull. Soc. Chim. France 1963 (12), 2814-20

Pryor Ltd.
Apparatus for Sulfur Recovery from Pyrites
British Patent 705,593 (1954), German Patent 934,584 (1955),
US Patent 2,821,461 (1958)

T. Rosenqvist and P. H. Hynne Reaction Between FeS and SO₂ Tidsskr. Kjemi, Bergvesen Met. 13, 196-200 (1953) (Eng.). CA 48, 6212f

H. Schackmann

Beispiele neuer Entwicklungen der Huttenkunde auf Grund Chemischer Forschung
Chem. Ing. Techn. 65-72 (1954)

N. G. Schmahl
The Iron-Sulfur-Oxygen System and Its Importance as a Basis for the Reactions of Iron Sulfides With Sulfur Dioxide to Form Iron Oxides and Sulfur Vapor. Archiv Eisenhüttenw. 25, 315-9 (1954). CA 48, 13392f

H. Suzuki

Chemical Reactions of Iron Sulfides. I. The Desulfurization of Pyrrhotite by Means of Sulfur Dioxide
Bull. Inst. Phys. Chem. Research (Tokyo) 22, 293-7 (1943). CA 42, 8689d

L. Wohler, F. Martin and E. Schmidt
The Formation of Sulfur by the Action of Sulfur Dioxide on Calcium Sulfide,
Zinc Sulfide and Iron Sulfide
Z. anorg. Chem. 127, 273-94 (1923). CA 17, 2403

3. Production of Sulfur via SO₂

R. F. Bacon and I. Benowitz

Elemental Sulfur from Roaster or Smelter Gases
US Patent 1,917,685 (1933)

R. F. Bacon and I. Benowitz Elemental Sulfur from Pyrites US Patent 1,917,234 (1933)

M. Berthelot

The Reactions Between Sulfur, Carbon, Their Oxides and Their Salts. Comp. rend. 96, 298-304 (1883)

E. P. Fleming and T. C. Fitt Reducing Sulfur Dioxide to Sulfur by Natural Gas US Patent 2,270,427 (1942)

E. P. Fleming and T. C. Fitt Recovery of Sulfur from Gaseous Mistures. US Patent 2,388,259 (1945). CA 40, 1000

E. P. Fleming and T. C. Fitt Production of Sulfur from Gaseous Mixtures US Patent 2,431,236 (1947)

E. P. Fleming and T. C. Fitt
High-Purity Sulfur from Smelter Gases. Reduction with Natural Gas.
Ind. Eng. Chem. 42, 2249-53 (1950)

R. A. King

Economical Utilization of Sulfur Dioxide from Metallurgical Gases Ind. Eng. Chem. 42, 2241-8 (1950)

R. Lepsoe

Chemistry of Sulfur Dioxide Reduction. Thermodynamics Ind. Eng. Chem. 30, 92-100 (1938)

R. Lepsoe

Chemistry of Sulfur Dioxide Reduction. Kinetics Ind. Eng. Chem. 32, 910-8 (1940)

R. Lepsoe and W. S. Kirkpatrick

Sulphur Dioxide Recovery at Trail

Trans. Can. Inst. Min. Met. 40, 399-404 (1937)

Pulp Paper Mag. Can. 39, 20-2, 54 (1938). CA 32, 3558

R. Lepsoe and J. R. Mills

Catalytic Reduction of Sulfur Dioxide to Sulfur US Patent 2 080 350 (1037)

US Patent 2,080,359 (1937)

A. R. Lindblad

Sulfur

British Patent 437,236 (1935)

D. Tyrer and Imperial Chemical Industries
Sulfur from Gases Containing Sulfur Dioxide

British Patent 358,580 (1930)

S. W. Young

Present Status of the Thiogen Process Eng. Mining J. 95, 369-70 (1913)

S. W. Young

Process for Reducing Sulfur Dioxide and Recovering the Sulfur US Patent 1,094,767 (1914)
Can. Patent 147,882 (1913)

M. A. Biswas, M. I. Ali and M. H. Khundar
Chlorination of Metal Sulfides. VI. Cadmium Sulfide, VII. Lead Sulfide
J. Indian Chem. Soc., Ind. & News Ed. 18, 225-30 (1955)

M. A. Biswas and M. H. Khundar Chlorination of Metallic Sulfides. II. Zinc Sulfide J. Indian Chem. Soc., Ind. & News Ed. 14, 29-35 (1951). CA 46, 49422

J. K. Chowdhury and K. M. Hossain
Recovery of Elemental Sulfur from Iron Pyrites
J. Indian Chem. Soc., Ind. & News Ed. 8, 81-93 (1945). CA 40, 6227

J. G. Donaldson and K. K. Kershner Chloridization of Certain Mineral Sulfides US Bur. Mines Dept. Invest. 6052 (1962)

V. I. Ezdakov Chlorination of Pyrite Sbornik Rabot Khim. 15, 131-3 (1939). CA 35, 4555

E. Hayek and T. Kraus Chlorination of Metal Sulfides Austrian Patent 167,098 (1950). CA 46, 7723a

R. L. Herrick
The Malm Dry Chlorination Process.
Mines and Minerals 30, 370-4 (1910)

H. Hohn, O. Horak and E. Schmiedl Working up Sulfide Iron Ores by Chlorination Austrian Patent 179,095 (1954). CA 48, 9303a

H. Hohn, G. Jangg, L. Putz and E. Schmiedl
Investigations on the Chlorination of Non-Ferrous Metal Ores
Proc. Intern. Mineral Dressing Congr. Stockholm 1957, pp. 683-700 (1958)

H. Hohn, H. Pranter and E. Schmiedl Working Up Sulfide Ores Austrian Patent 189,799 (1957). CA 51, 9461b

S. A. Ionides
The Dry Chlorination of Complex Ores
Mining Sci. Press, 112, 781-7 (1916). CA 10, 1975

- K. K. Kershner and J. G. Donaldson Chloridizing the Sulfides of Lead, Zinc and Copper US Bur. Mines Rept. Invest. 5894 (1961)
- S. S. M. A. Khorasani, S. M. Hasan, and M. H. Khundkar Reaction Between Antimony Trisulfide and Ferric Chloride Pakistan J. Sci. Res. 15 (2), 60-4 (1963)
- M. H. Khundkar and S. J. Quadr Chlorination of Metal Sulfides. III and IV. Cuprous Sulfide J. Indian Chem. Soc., Ind. & News Ed. 14, 85-9, 90-4 (1951). CA 46, 4943a
- S. I. Levy and G. W. Gray Treating Iron Pyrites British Patent 307,190 (1928). CA 23, 5150
- G. C. Mitter

 An Integrated Plan For Copper and Sulfur Extraction From Copper Pyrites Indian Min. J., 5, 184-5 (1957) (Special Issue)

J. Muller

German Patent 406,673 (1924)

- V. Pristoupil
 Preparation of Zinc Chloride by a Thermic and Chlorination Process Chem. Obzor. 12, 135-9 (1937). CA 31, 8127
- R. C. Rowe Sulfur from Pyrites Can. Min. J. 59, 181-3 (1938)
- A. G. Starliper and H. Kenworthy
 Recovery of Lead and Sulfur by Combined Chlorination and Electrolysis of Galena
 US Bur. Mines, Rept. Invest. 6554 (1964)
- O. J. Steinhart
 Chlorine Smelting. Discussion on Swinburne's Paper
 Mining Sci. Press, 87, 352 (1903)

J. Swinburne

Chlorine Smelting with Electrolysis Trans. Faraday Soc. (1903) Mining Sci. Press 87, 82, 90 (1903)

F. W. Traphagen
Dry Chlorination of Sulfide Ores
Mining Sci. Press 98, 522 (1909)

G. G. Urazov, I. S. Morozov and G. U. Ustavshckikova Experimental Investigation of Chloridization of Copper-Nickel and Iron-Bearing Matte Tsvetn. Metal. 10 (6), 109-130 (1935). CA 30, 8109

E. Zielinski

Investigation of the Conditions for the Chloridizing Volatilization of Metals.

Arch. Erzbergbau Erzaufbereit. Met. 1, 31-41 (1931). CA 28, 437

HYDROMETALLURGICAL METHODS

I. Production of Sulfur via H₂S

R. Bacon
Sulfur from Sulfides
US Patent 1,897,921 (1933). CA 27, 2770

W. Lindenlaub

The Production of Electrolytic Zinc from Zincblende Containing Iron and Silica Metallurgie u. Giessereitech. 4, 225-7 (1954). CA 48, 13576c

F. Pawlek and H. Pietsh
Anwendug des Druckaufschlusses auf Erze und Huttenzwischenprodukte
Z. Erzbergbau Metallhuttenw. 10, 373-83 (1957)

M. Rajagopalan and D. Waldie and Co. Extraction of Zinc and Sulphur Indian Patent 52,381 (1955). CA 50, 3987a

O. C. Ralston and C. R. Kuzell
Treating Copper Mattes
British Patent 355,078 (1931). CA 26, 2955
Canadian Patent 315,514 (1931). CA 26, 1563

A. M. Sébillot and G. P. Dubois
Treating Copper Containing Pyrite
French Patent 384,072 (1907). CA 3, 1393

K. Teufel
Metallurgy
German Patent 494,633 (1925). CA 24, 3478

2. Aqueous Oxidation of Sulfide Ores

R. B. Bhappu, D. H. Reynolds and W. S. Stahman
Studies on Hypochlorite Leaching of Molybdenite
Proc. AIME Symposium "Unit Processes in Hydrometallurgy", Dallas 1963,
Gordon and Beach, New York pp. 95-113 (1965).

K. W. Downes and R. W. Bruce
The Recovery of Elemental Sulfur from Pyrite and Pyrrhotite
Trans. Can. Inst. Min. Met. 53, 77-82 (1955)

F. A. Forward et al. Method for Treating Pyrrhotitic Mineral Sulfides Containing Non-Ferrous Metal Values for the Recovery of Said Metal Values and Sulfur US Patents 2,898,196 and 2,898,197 Canadian Patent 547,012

F. A. Forward and H. Veltman
Direct Leaching Zinc-Sulfide Concentrates by Sheritt Gordon
J. Metals 11, 836-840 (1959). US Patent 2,996,440 (1961)

F. A. Forward, H. Veltman, and A. Vizsolyi
The Direct Oxidation of Galena in Acid Solutions
Intern. Mineral Processing Congress, London 1960.

A. D. Hadsel
Chlorination of Complex Sulfide Ores
US Patent 2,697,034 (1954). CA 49, 15,713e

K. J. Jackson and J. D. H. Strickland
The Dissolution of Sulfide Ores in Acid Chlorine Solutions; A Study of the More Common Sulfide Minerals.
Trans. Met. Soc. AIME 212, 373-9 (1958)

V. N. Mackiw and H. Veltman
Acid Leaching of Copper from Chalcocite Mixed with Pyrite
Canadian Patent 712,989 (1965)

D. R. McKay and J. Halpern
A Kinetic Study of the Oxidation of Pyrite in Aqueous Suspension
Trans. Metall. Soc. AIME 212, 301-309 (1958)

Minister of Mines and Technical Surveys of Canada Sulfur from Sulfides of Iron British Patent 722,143 (1955). CA 49, 16372b

S. Nashner and F. A. Forward Sulfur Recovery Canadian Patent 683,663 (1953)

F. Pawlek and H. Pietsch
Anwendung des Druckaufschlusses auf Erze und Huttenzwischenprodukte.
Z. Erzbergbau Mettallhuttenw. 10, 373-383 (1957)

<u>V. Pristoupil</u>
The Wet Chlorination Process for the Preparation of Zinc Chloride Chem. Obzor. <u>12</u>, 217-21 (1937). CA <u>32</u>, 9408

<u>J. Rygaert, J. Saelemaekers</u> and <u>A. Van Tiggelen</u> Lixiviation Orydante du Sulfure de Cuivre Bull. Soc. Chim. Belg. <u>68</u>, 19-29 (1959)

M. I. Sherman and J. D. H. Strickland
Dissolution of Lead Sulfide Ores in Acid Chlorine Solutions
Trans. Met. Soc. AIME 209, 795-800 (1957)

M. I. Sherman and J. D. H. Strickland
Dissolution of Pyrite Ores in Acid Chlorine Solutions
Trans. Met. Soc. AIME 209, 1386-8 (1957)

F. W. Traphagen
Chlorinating Complex Sulfide Ores Such as Those Containing Zinc and Other Metals
US Patent 2,017,330 (1935). CA 29, 7928

ELECTROLYTIC METHODS

1. Electrolysis of Molten Sulfides

G. Angel and E. Garnum

Production of Lead and Sulfur from Galena by Electrolysis of Fused Masses
Tek. Tid. 75, 279-84 (1945). CA 40, 6345

I. T. Gul'din, V. P. Buzhinskaya, V. P. Burseg'yan, and V. K. Ruppul Electrolysis of Lead Concentrates in Fused Salts Zh. Prikl. Khim. 33, 378-83 (1960). CA 54, 1059ld, 53, P 929f

I. T. Gul'din et al.

Lead and Sulfur from Sulfidic Lead Concentrates and an Electrolyzer for the Process

USSR Patent 112,489 (1958). CA 53, 929f

T. P. Hoar and R. G. Ward
The Production of Copper and Sulphur by the Electro-Decomposition of Cuprous Sulphide.
Trans. Inst. Min. Met. (London) 67, 393-410 (1958)

N. A. Izgaryshev and N. K. Grigor'ev

Electrodeposition of Lead and Zinc from Fused Salts
J. Gen. Chem. USSR 6, 1676-85 (1936). CA 31, 2101

R. Kammel

Schmeltzflusselektrolytische Gewinnung von Blei und Antimon aus Sulfidischen Konzentraten.

Z. Erzbergbau Metallhuttenw. 14, 497-552 (1961)

National Smelting Company Itd. British Patent 448,328 (1934) Belgian Patents 406,053 (1934)

and 411,841 (1935)

Yugoslav. Patent 12,697 (1935)

German Patent 651,132 (1937)

J. B. Richardson

A Revival of Lead Mining at Halkyn, North Wales Bull. Inst. Min. Met. 387 (1936)

W. Savelsberg

Über die Elektroyse geschmolzener Metallsulphide Z. Elektrochem. 46, 379-97 (1940). CA 35, 958

P. Simonds

Electrolytic Reduction of Galena in Fused Salt Thesis T 704, Misscuri Sch. Mines 1940, 52 pp.

J. Swinburne

Elektrolytische Zerlegung sulfidischer Erze in einem Bad geschmolzener Chloride unter Abscheidung von Metall und Schwefel German Patent 134,734 (1898)

C. P. Townsend

German Patent 182,476 (1906) 815,881 (1906) US Patent

W. Truthe

Über das Verhalten der Sulfide von Pb, Cu, Ag and Cu₂O in der Schmelzen der Zugehörigen Chloride

Z. anorg. Chem. <u>76</u>, 161-173 (1912). CA <u>6</u>, 2372

W. Valentine and A. G. Betts

US Patent 816,764 (1906)

R. Vivian

Electrolysis of Molten Antimony Sulfide Trans. Electrochem. Soc. 69, 657-60 (1936) H. Winterhager
Electrochemical Fundamentals of the Fusion Electrolysis of Lead Sulfide in Melts Containing Lead Chloride
Forschungsber. Wirtsch.-u. Verkehrsministeriums Nordrhein-Westfalen,

No. 134, 42 pp. (1955). CA 53, 7824h

H. Winterhager and R. Kammel
Electrochemical Basis for the Electrolysis of Lead Sulfide in Fused
Electrolytes
Z. Erzbergbau Metallhuttenw. 9, 97-105 (1956). CA 50, 8347g

2. Electrolysis of Sulfide Anodes in Aqueous Phase

Anonymous
Sulfide Anode Cancels Sinter and Smelt; Nickel Process Pioneers Sulfur Distillation
Chem. Eng. 65 (4), 60-2 (1958)

Anonymous
Direct Electrolysis of Nickel Matte
Can. Chem. Proc. 42, 72-74, 76, 78 (1958)

I. Bernfeld
Studien über Schwefelmetallelektroden
Z. physik. Chem. 25, 46-73 (1898)

J. A. W. Borchers, P. R. Franke and F. E. Gunther Process for the Electrolytic Production of Copper US Patent 830,639 (1906)

P. B. Bryk and S. A. Aarnisalo Electrolytic Purification of Nickel from Nickel Matte Swedish Patent 124,283 (1949). CA 43, 8919h

D. M. Chizhikov, N. A. Gurovich, B. Z. Ustinskii, Z. F. Gulyanitskaya, B. P. Kreigauz, I. N. Kitler and L. V. Pliginskaya

Electrolytic Conversion of Cu-Ni-Co Matte

USSR Patent 158,074 (1963). CA 60, P 10222h

D. M. Chizhikov and B. Z. Ustinskii Electrochemical Solution of Metal Sulfides Izvest. Akad. Nauk. SSSR, Otdel. Tekh. Nauk. 1948, 229-234. CA 42, 6675i

D. M. Chizhikov and B. Z. Ustinskii Electrochemical Solution of Sulfide Alloys Izvest. Akad. Nauk. SSSR, Otdel. Tekh. Nauk, 1949, 1481-92

D. M. Chizhikov and B. Z. Ustinskii Investigation of Anodic Polarization of Sulfides of Copper and Nickel and of some of their Alloys Zh. Priklad. Khim. 29, 1129-31 (1956). CA 50, 16474h

V. Engelhardt
Handbuch der Technichen Elektrochemie Bd. I, II.Teil A, Die technische Elektrolyse wässriger Losungen
page 90. Akademische Verlaggesellschaft, Leipzig 1932.

N. S. Fortunatov and V. Mikhailovaskaya Anodic Solution Potentials of Metal Sulfides Ukrain. Khim. Zh.16, 667-81 (1951). CA 48, 2497c

M. A. Klochko and M. E. Mironova Anodic Dissolving of Copper-Sulfur Alloys Izvest. Sektora Fiz. Chim. Anal. Inst. Obschei i Neorg. Khim., Akad. Nauk SSSR 25, 128-33 (1954). CA 49, 14527h

M. A. Klochko and M. E. Mironova Anodic Behavior of Alloys of Palladium-Sulfur. Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk SSSR 26, 68-75 (1955).

M. A. Klochko and M. E. Mironova Anodic Behavior of a Triple Alloy of Copper, Palladium, and Sulfur Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk SSSR <u>26</u>, 75-81 (1955). CA <u>50</u>, 2320a

M. Loshkarev, O. Esin and G. Lapp Electrolysis of Nickel Matte Zh. Prikl. Khim. 18, 294-300 (1945). CA 40, 3343

Marchese

German Patent 22,429 (1882)

L. S. Renzoni, R. C. McQuire and M. V. Baker Direct Electrorefining of Nickel Matte J. Metals 10, 414-8 (1958)

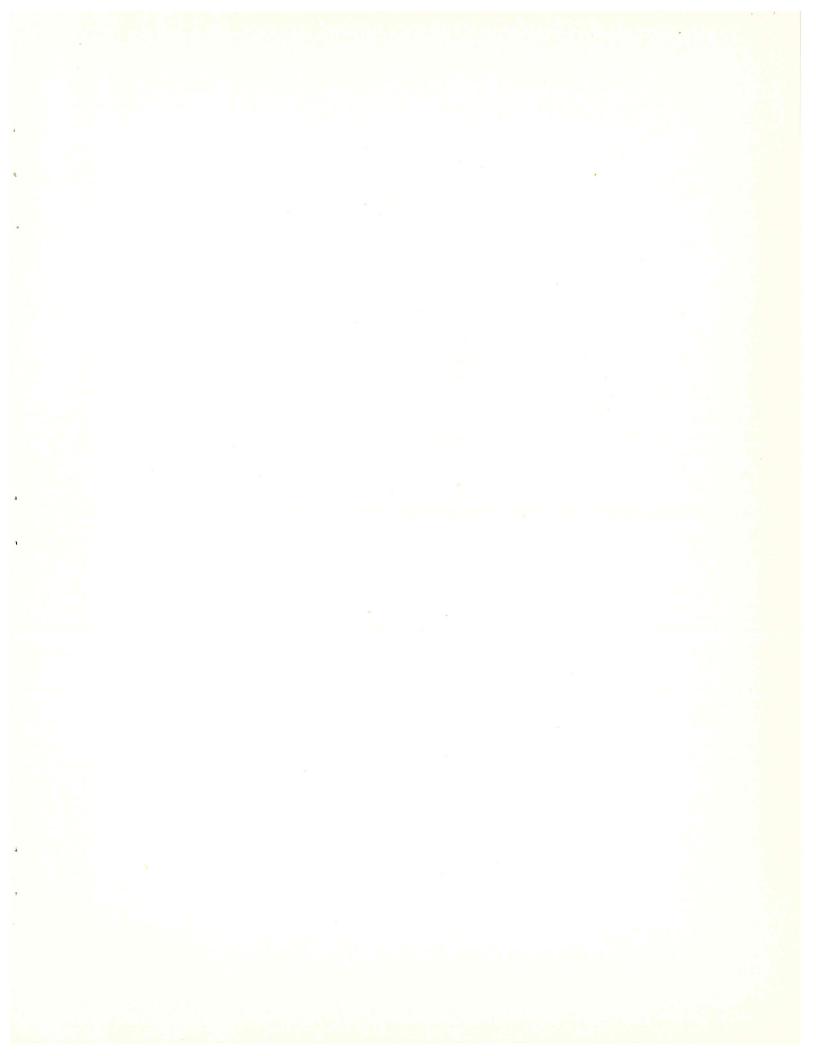
A. L. Rotinyan
The History of Electrolysis of Sulphide Nickel Anodes
Tsvetn. Metal. 32 (4), 88 (1959)

W. W. Spence and W. R. Cook
The Thompson Refinery
Trans. Can. Min. Met. 67, 257-67 (1964)

B. Z. Ustinskii and D. M. Chizhikov
Potentials of Metal Sulfides and Their Alloys
Zh. Priklad. Khim. 22, 1249-52 (1949). CA 44, 3816i

J. Egli Studien zur Theorie der Elektrolytischen Kupfergewinnungsmethoden. Z. anorg. Chem. 30, 18-85 (1902)

		3
		d
		κ,
		P
		6
		C



THE MONTANA BUREAU OF MINES AND GEOLOGY IS A PUBLIC SERVICE AGENCY FOR THE STATE OF MONTANA. ITS PURPOSE IS TO ASSIST IN DEVELOPING THE STATE'S MINERAL RESOURCES. IT CONDUCTS FIELD STUDIES OF MONTANA GEOLOGY AND MINERAL DEPOSITS, INCLUDING METALS, OIL AND GAS, COAL, OTHER NON-METALLIC MINERALS, AND GROUND-WATER. IT ALSO CARRIES OUT RESEARCH IN MINERAL BENEFICIATION, EXTRACTIVE METALLURGY, AND ECONOMIC PROBLEMS CONNECTED WITH THE MINERAL INDUSTRY IN MONTANA. THE RESULTS OF THESE STUDIES ARE PUBLISHED IN REPORTS SUCH AS THIS.

FOR FURTHER INFORMATION, ADDRESS THE DIRECTOR, MONTANA BUREAU OF MINES AND GEOLOGY, MONTANA COLLEGE OF MINERAL SCIENCE AND TECHNOLOGY, BUTTE.