Mines Branch Information Circular IC 242

THE HYDROGEN SULPHIDE ROUTE TO SULPHUR RECOVERY FROM BASE METAL SULPHIDES

PART I: THE GENERATION OF H_2S FROM BASE METAL SULPHIDES

by

H.W. Parsons* and T.R. Ingraham**

ABSTRACT

Papers and patents published in the past sixty years have been selectively reviewed as part of a project for determining the feasibility of recovering hydrogen sulphide from base metal sulphides. The most promising reactions involve pyrrhotite and a warm aqueous solution of hydrochloric acid. Simultaneous separate reviews have been made of means for converting hydrogen sulphide to elemental sulphur and of recovering an iron product from the ferrous chloride solutions.

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*Research Scientist and **Head, Research Section, Extraction Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

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RÉCUPÉRATION DU SOUFRE DES SULFURES DE MÉTAUX COMMUNS PAR LA VOIE DE L'ACIDE SULFHYDRIQUE

PARTIE I: PRODUCTION DE H_2S À PARTIR DES SULFURES DE MÉTAUX COMMUNS

par

H.W. Parsons* et T.R. Ingraham**

RÉSUMÉ

Les auteurs ont étudié une sélection de mémoires et de brevets publiés au cours des 60 dernières annees en vue de déterminer la possibilité de récupérer l'acide sulfhydrique à partir des sulfures de métaux communs. Les réactions les plus prometteuses sont obtenues à l'aide de la pyrrhotine et d'une solution aqueuse chaude d'acide chlorhydrique. D'autres études complémentaires ont porté sur divers moyens de transformer l'acide sulfhydrique en soufre élémentaire et de récupérer un produit du fer des solutions de chlorure ferreux.

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*Chercheur scientifique et **Chef, Section de la recherche, Division de la métallurgie extractive, Direction des mines, ministere de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

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INTRODUCTION

In one of its aspects, the Mines Branch Environmental Improvement Program is concerned with the reduction of sulphur dioxide pollution of the air utilized for the combustion of fossil fuels and for the pyrometallurgical treatment of sulphide minerals. The Program at the present time involves a multifaceted attack on the problems associated with both of these major sources of sulphur dioxide emissions.

In this report series on "The Hydrogen Sulphide Route to Sulphur Recovery from Base Metal Sulphides", an examination is made of the various steps that might be involved in recovering sulphur directly from sulphide minerals via the intermediate step of generating hydrogen sulphide. The hydrogen sulphide route was selected for study because of its inherent flexibility. Sulphur may be recovered directly from hydrogen sulphide by the Claus reaction, in which the H_2S is oxidized with precisely the stoichiometric amount of oxygen:

$$2H_2S + O_2 \rightleftharpoons 2H_2O + 2S \qquad [1]$$

Or, as an alternative, the H_2S may be used to reclaim the sulphur from the sulphur dioxide produced by pyrometallurgical methods of treating sulphide ores:

$$2H_2S + SO_2 \rightleftharpoons 2H_2O + 3S \qquad [2]$$

The technology for sulphur recovery from hydrogen sulphide is well established. The reactions are virtually quantitative and they are effective with both strong and dilute gas mixtures.

The inherent flexibility of the hydrogen sulphide route for producing sulphur is attractive at the present time when attempts are being made to reduce sulphur dioxide pollution levels.

In this series of reports, the methods of generating hydrogen sulphide from sulphide ores are examined and, based on the assumption that the chloride systems are favoured, an examination is made of the methods of recovering iron products and of regenerating hydrogen chloride. In a third report of the series a detailed examination is made of the Claus reaction and the variety of its applications.

This particular report reviews the methods of generating hydrogen sulphide from sulphide ores.

METHODS FOR GENERATING H_2S FROM SULPHIDES

Although H_2S may be generated from base metal sulphides by various means, the only methods pertinent to this discussion are those that show some promise of evolving into practical processes. They may be classed as "wet" methods, that involve the leaching of sulphides with non-oxidizing acids, or as "dry" methods, in which gases react with the sulphides under non-oxidizing conditions.

The extraction of metals from sulphide ores by wet methods was extensively reviewed (142 references) by Forward and Warren(1) in 1960. They observed that most of the work up to the mid-20th century was done for the purpose of sulphating the metals with sulphuric acid. In those processes the sulphide was released as H_2S. From approximately 1950 onwards, the use of other reagents, such as ammonia, came into prominence. The techniques of high-pressure metallurgy were also developed then. The physical, chemical and technological principles underlying the application of high-pressure and high-temperature techniques to hydrometallurgy were discussed by Forward and Halpern(2). Both of their papers emphasize the variety of forms in which the sulphur from the sulphide may emerge as a result of treating the minerals.

Depending on the starting materials and the conditions employed, sulphur in the sulphide can react to form one or more of: elemental sulphur, hydrogen sulphide, sulphur dioxide, polysulphides, thiosulphate, thionates, sulphamates, or sulphates(3).

This review pertains only to the generation of H_2S. Those processes which produce sulphur in any other form are not reviewed. Processes in which H_2S appears as an intermediate product are also omitted from this discussion. The precise mechanism of the oxidation of sulphide ion or H_2S to elemental sulphur or sulphate is not known as yet(1)(3)(4)(5).

Processes which evolve H_2S and/or sulphur as a minor constituent of the off-gases are not discussed in this review. An example of such a process is the flash-smelting treatment of pyrite at Outokumpu Oy, in Finland(6)(7).

GENERAL REMARKS ON THE LEACHING OF SULPHIDES

Halpern(8) discussed the principles of physical chemistry that underlie hydrometallurgical processes. He noted that although the operational aspects of many hydrometallurgical process are well known, in many cases a detailed understanding of the physical chemical principles which govern their operation has not been achieved. He observed that the progress towards the understanding of the mechanism of leaching of sulphides has been slower than that for systems involving metals or oxides. This was because of the more complex chemistry of the leaching of sulphides. Forward and Warren(1) described several factors which complicate the chemistry of sulphide leaching, among which are the diversity of structures of the metal sulphides, the changes in structural formula undergone by many of the sulphides on leaching, and the large variety of sulphur products formed.

Some of the differences in the leaching behaviour of different sulphides, or of different samples of the same sulphide, were attributed by Forward and Warren(1) to the variety of different structures permitted by the metal-sulphide bonds. These bonds are essentially co-valent in character, but their bonding electrons do not behave as in simple co-valent crystals. One well-known example of the diversity of sulphide structures is that of pyrite. Unlike the majority of sulphides, pyrite contains sulphur-to-sulphur bonding. Because of this, the mechanism of its reactions differs from those of other sulphides that lack an S-S bond. Forward and Warren(1) observed that because each sulphide differs from every other sulphide, the particular conditions necessary to treat a specific starting material must be empirically determined by experimentation, and only general chemical principles can be used as a guide.

Another complicating factor is the change in composition of the sulphides during leaching. For example, Thomas and his co-workers(9) found that chalcocite (Cu_2S) was progressively converted by concurrent reactions into djurleite ($Cu_{1.96}S$), digenite ($Cu_{1.8}S$), blaubleinder covellite ($Cu_{1.1}S$), and normal covellite (CuS), during leaching. Eliseev and Smirnova(10) studied the progressive changes in the composition of pentlandite that resulted from treatment of the mineral with hydrochloric acid. The fact that pentlandite dissolved only partially at comparatively low temperatures (up to 60°C), whereas at higher temperatures dissolution was almost complete, was attributed to changes in composition and physical properties of the mineral.

Finally, as has been noted previously, the variety of sulphur products formed by the sulphide complicates the chemistry of the leaching of sulphide minerals. Majima and Peters(3) summarized the thermodynamic considerations in the potential-pH diagram shown in Figure 1. A discussion of this diagram with its predictions of the products to be expected under different circumstances is included in the next section.

THERMODYNAMICS

Although there is sufficient tabulated thermodynamic data available for calculations to be made for most hydrometallurgical systems, most of the data are for room temperature. Halpern(8) remarks on the need for more reliable data at higher temperatures, more data on the activities of salts in concentrated solutions, and more information on the thermodynamic properties of complex ions. Under the sponsorship of the International Copper Research Association, some of the required data are now being generated and correlated by Professor Duby of Columbia University. Halpern(8) observes that, in general, knowledge of the thermodynamics of hydrometallurgical reactions is more advanced than knowledge of their kinetics and mechanisms.

Many hydrometallurgical systems have been represented by Pourbaix and others in the form of potential-pH diagrams(11-17). These diagrams are a visual representation of the relevant thermodynamic data. They are an aid in determining the conditions required to stabilize a given species, and in predicting the change in products that may be expected from a change in conditions. Halpern(8) considers the diagrams to be aids in understanding the thermodynamic problems encountered in leaching processes.

Over the years, many investigations have been conducted into the leaching of sulphides, with both sulphuric and hydrochloric acids. Majima and Peters(3) studied the reactions of a variety of minerals - pyrite, pyrrhotite, chalcopyrite, chalcocite, covellite, bornite, galena, sphalerite, and stibnite - under various leaching conditions. They summarized the free energies of reaction as shown in Table 1.

TABLE 1. Free Energy of Hydrogen Sulphide Formation from Some Sulphides in Acid Solution

	ΔG°_{298}, kcal per mole
(1) $FeS + 2H^+ \rightleftharpoons Fe^{++} + H_2S(g)$	-4.872
(2) $FeS_2 + 2H^+ \rightleftharpoons Fe^{++} + H_2S(g) + S^\circ$	+11.648
(3) $ZnS + 2H^+ \rightleftharpoons Zn^{++} + H_2S(g)$	+4.324
(4) $PbS + 2H^+ + SO_4^{--} \rightleftharpoons PbSO_4 + H_2S(g)$	-2.29
(5) $Cu_2S + 2H^+ \rightleftharpoons Cu^{++} + Cu^\circ + H_2S(g)$	+28.4
(6) $CuS + 2H^+ \rightleftharpoons Cu^{++} + H_2S(g)$	+19.34

The conditions for recovering various sulphur products during the leaching of sulphides are shown in Figure 1, in which the electrode potential is plotted against the pH for the sulphur system.

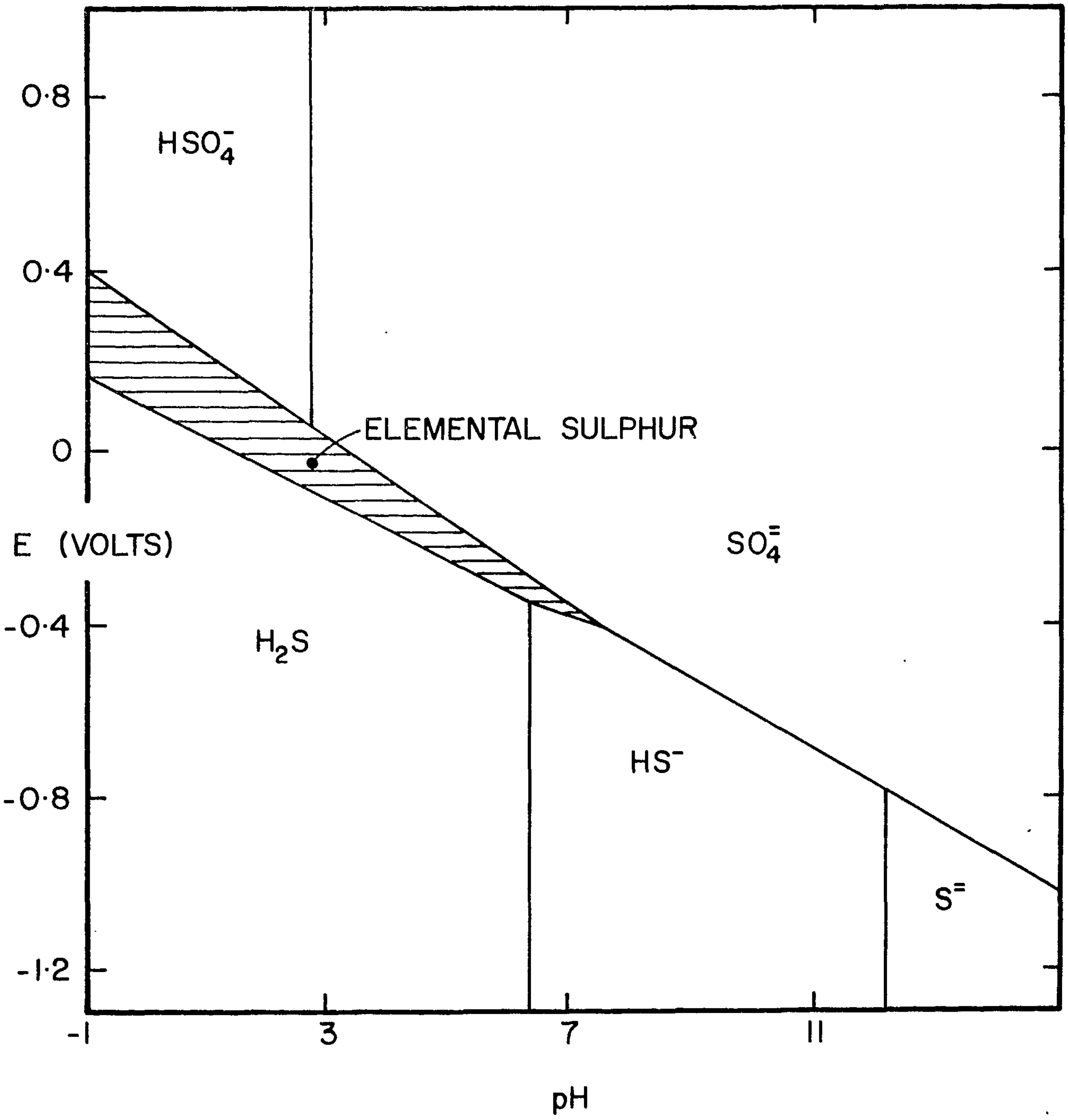


FIGURE 1: Potential-pH diagram for sulphur at 100°C

The diagram in Figure 1 shows only those species of sulphur which are stable in appreciable quantity at 100°C, i.e. sulphate ion, bisulphate ion, elemental sulphur, hydrogen sulphide, bisulphide ion, and sulphide ion.

The area in the lower right-hand corner of the diagram is that for the sulphide ion and is enclosed by lines representing the reactions:

$$H^+ + S \rightleftharpoons HS^- \qquad [3]$$

and

$$S^= + 4H_2O \rightleftharpoons 8H^+ + SO_4^= \qquad [4]$$

The diagram shows that at 100°C when the pH is less than about 12.1, free sulphide ion ceases to exist in solution. Instead, it combines with H^+ to form HS^-. At 100°C and when the pH is less than about 6.2, the HS^- ion ceases to exist as a significant species. Hydrogen sulphide is the form of sulphur in systems where the solution potential is less than about -0.35 V. If the potential is increased, the stable product is no longer H_2S but elemental sulphur. The boundary conditions for the recovery of elemental sulphur are those shown as enclosing the cross-hatched area on the diagram. In neutral solutions, at all potentials greater than about -3.5 V, the only stable sulphur species is the sulphate ion. The bisulphate ion is stable only below pH 2 in solutions where the potential is greater than about 0.1 V.

Experiments have shown(3) that at temperatures below 110°C, an almost quantitative conversion to elemental sulphur is obtained from galena, from pyrrhotite, and from sphalerite, but not from pyrite or the copper minerals. The sulphur that is not converted to elemental sulphur in acid solutions appears as sulphate salts or sulphuric acid. Higher temperatures favour formation of sulphate relative to elementary sulphur; generally speaking, higher acidity results in more sulphur being formed relative to sulphate. Experiments have shown that for different minerals sulphur is formed at different pH values(1).

A potential-pH diagram, shown in Figure 2, was used by Yazawa(18) to illustrate the selective leachability of mineral sulphides. The diagram should be interpreted with care because it is prepared for pH values to -6. Any value less than -1 is likely to be impossible to attain in any practical system. Pazdnikov(107) suggested that selective leaching of complex sulphide ores should be possible when there is a difference between the potentials of the metals composing the ore.

The equilibrium in sulphide-chloride systems in aqueous solutions was studied by Tarabaev and his co-workers(19). They experimented with synthetic sulphides at room temperature and at 80°C, in the presence and absence of NaCl. Their conclusion was

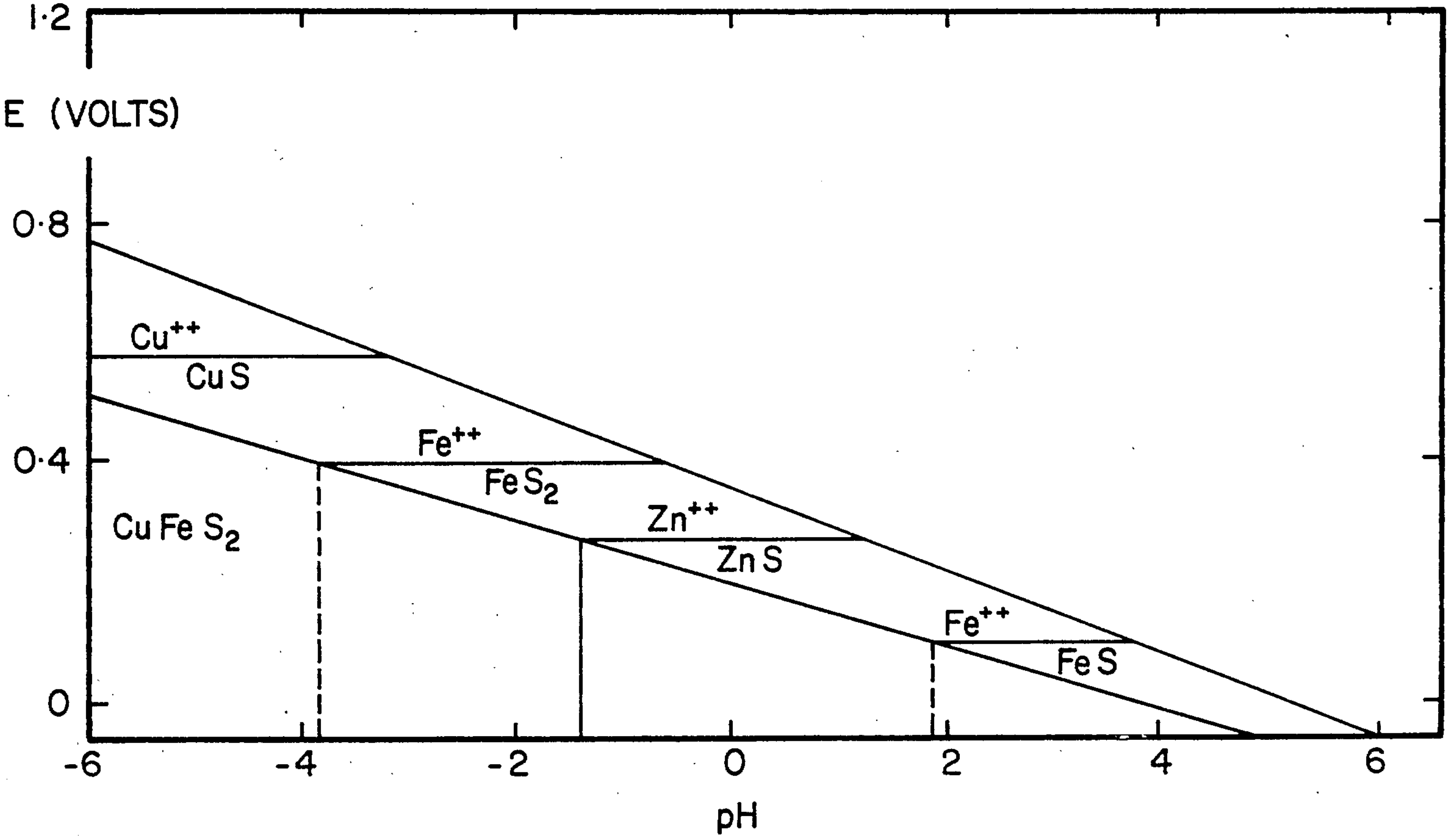


FIGURE 2: Potential-pH diagram for explaining selective leaching process

that the solubility of metals in this system was proportional to the ratio, $[HCl]^2/[H_2S]$. They obtained the equilibrium constants shown in Table 2.

TABLE 2

The Variation of Equilibrium Constant with Temperature and the Presence of NaCl

Reaction	Equilibrium Constants		
	at 80°C, no NaCl	at 80°C, 300 g/l NaCl	at 20°C, 300 g/l NaCl
(1) $ZnS + 2HCl \rightleftharpoons ZnCl_2 + H_2S$	0.0432	4.32	0.213
(2) $FeS + 2HCl \rightleftharpoons FeCl_2 + H_2S$	0.778	1.97	0.09
(3) $PbS + 2HCl \rightleftharpoons PbCl_2 + H_2S$	0.00012	0.091	0.009
(4) $CdS + 2HCl \rightleftharpoons CdCl_2 + H_2S$	0.00028	0.0545	0.00606
(5) $Sb_2S_3 + 6HCl \rightleftharpoons 2SbCl_3 + 3H_2S$	0.307×10^{-12}	0.166×10^{-10}	0.149×10^{-11}

Tarabaev et al.(19) found that the solubility of all the sulphides (especially PbS) increased in the presence of NaCl. From their data they concluded that it was possible to leach Pb, Zn, Fe and Cd from sulphide ores and concentrates with weakly acid solutions and thus separate these metals from the copper mineral that remained in the residue.

PATENTS AND PROCESSES

There are many references in the literature to methods for generating H_2S from mineral sulphides. An early method, popular in the mid-1920's prior to the advent of differential flotation, was the brine leaching of ores containing lead. Typical patents were filed by Christensen(20-31), in which he mentioned the inhibitory effect of the evolved H_2S, and the necessity of agitation to rid the solution of this gas. Christensen's patents were the basis for the commercial Snyder-Christensen Process(32), used by the National Lead Company, to treat complex sulphide ores in a 200-ton-per-day pilot plant. The plant was not successful, because of operating difficulties, one of which was the disposal of the large quantities of hydrogen sulphide gas produced.

Recent interest in the brine leaching process is shown by Russian studies(33)(34). In 1963 Tarabaev(33) leached zinc and lead separately from a bulk flotation concentrate, and in 1968 Ermilov and his co-workers(34) used the same mixture - HCl and $CaCl_2$ brine - in a pilot-plant process for treating a complex copper-zinc-lead sulphide concentrate.

There are many references to the treatment of sulphide minerals with acids to generate hydrogen sulphide gas. Typical patents are those of Christensen, who leached lead and zinc sulphide ores with hot concentrated hydrochloric acid, to convert the zinc sulphide to zinc chloride(35)(36). The mixture was heated, excess acid was driven off, and the zinc chloride was extracted from the residue with water.

In other patents, Christensen(37,38,39) described methods in which the ore was ground with an excess of hot sulphuric acid. With lead ores, the $PbSO_4$ was leached with a calcium chloride brine(37); zinc sulphate formed during the treatment of zinc ores was leached with water(38)(39)(40)(41). In the treatment of zinc-lead ores, Christensen(42-44) also regulated the concentration of the sulphuric acid to avoid dissolving the sulphated zinc(41)(42)(43), while a sufficient amount was added to sulphate all the lead and zinc(44).

A Japanese patent(45) described the dissolution of zinc from a copper sulphide ore by leaching with H_2SO_4 ; the remaining residue was differentially floated into sulphide concentrates of lead, copper and iron.

Many references in literature cite the treatment of matte; Tobleman(46) believed that the cheapest way of generating hydrogen sulphide was by the action of sulphuric acid on a low-grade copper matte. An early patent(47) described the treatment of a raw or slightly roasted Cu-Ni matte with a suitable quantity of acid at high temperatures and pressure to liberate H_2S and produce solutions of nickel chloride or sulphate free from copper. This patent specified that if the matte were roasted, enough NiS must be left unoxidized to provide for the precipitation of all the copper. The roasting of a Cu-Ni matte until it contained 8-12% sulphur, followed by reduction by gases, coke, or some other means prior to leaching, was recommended in another patent(48).

The importance of the amount of sulphur in the matte is illustrated by the emphasis that the patents place on this point. For example, one patent(49) specified that a Ni-Cu or Co-Cu matte must have a sulphur content of less than one-third and more than one-fifth of the copper content; another(50) described the sulphur content to be one-quarter that of the copper content. This patent also recommended the use of a 20% hydrochloric acid solution; earlier patents by Wells(51,52) called for at least a 25% solution of hydrochloric acid.

The time required to dissolve the nickel from a Cu-Ni matte depended upon a number of factors. One patent(53) stated that a matte, treated with hydrochloric acid diluted to contain from ten to thirty percent acid, took from one to ten hours to dissolve the nickel content. The length of time was determined by the quantity of matte, its chemical composition and physical condition, the strength and amount of acid used, the amount of agitation used, and the amount of heat applied during the treatment. It was recommended that the size of the material should be 60 mesh or finer and that the operating temperature be between 110° and 210°F. In his proposed nickel refining process, Lathe(54) found that a very fine crystalline structure favoured rapid solution of the nickel. He therefore simultaneously cooled and granulated the matte by pouring the hot material into cold water. Lathe(54) found that well granulated matte, ground to minus 80 mesh, leached with concentrated sulphuric acid for three hours at a temperature of 80°C-100°C, yielded a residue which contained only 0.2 percent nickel. He thus obtained, in one simple operation, a separation of about 99.8 percent of the nickel from 100 percent of the copper and precious metals in the matte.

The leaching of mattes has been studied in Russia. Kryukova(55) investigated the leaching of nickel mattes with a hydrochloric acid solution. Govorov(56) investigated the hydrometallurgical treatment of copper-nickel mattes by two-stage, counter-current leaching with H_2SO_4. The results of his experiments showed that iron was extracted as $FeSO_4$ in the first stage of a leach in a neutral solution containing no non-ferrous and associated metals. In this first stage of leaching, 70% of the sulphur was evolved as H_2S. The nickel, cobalt and residual iron were leached from the residue in the second stage, in which fresh H_2SO_4 was used. The copper remained in the residue. Govorov(56) claimed that good separation was possible only with mattes in which the ratio of iron to nickel was equal to, or greater than, 3.5:1, the sulphur content was equal to or less than 29%, and the magnetite content of the matte was less than or equal to 2%.

A relatively recent example of a promising process for the treatment of mattes is described in a patent filed by Thornhill(57). In this process, the flowsheet for which is shown in Figure 3, a copper-nickel Bessemer matte is leached with hydrochloric acid to separate nickel, as the chloride, from the copper which remains in the residue. From the leaching tanks the evolved

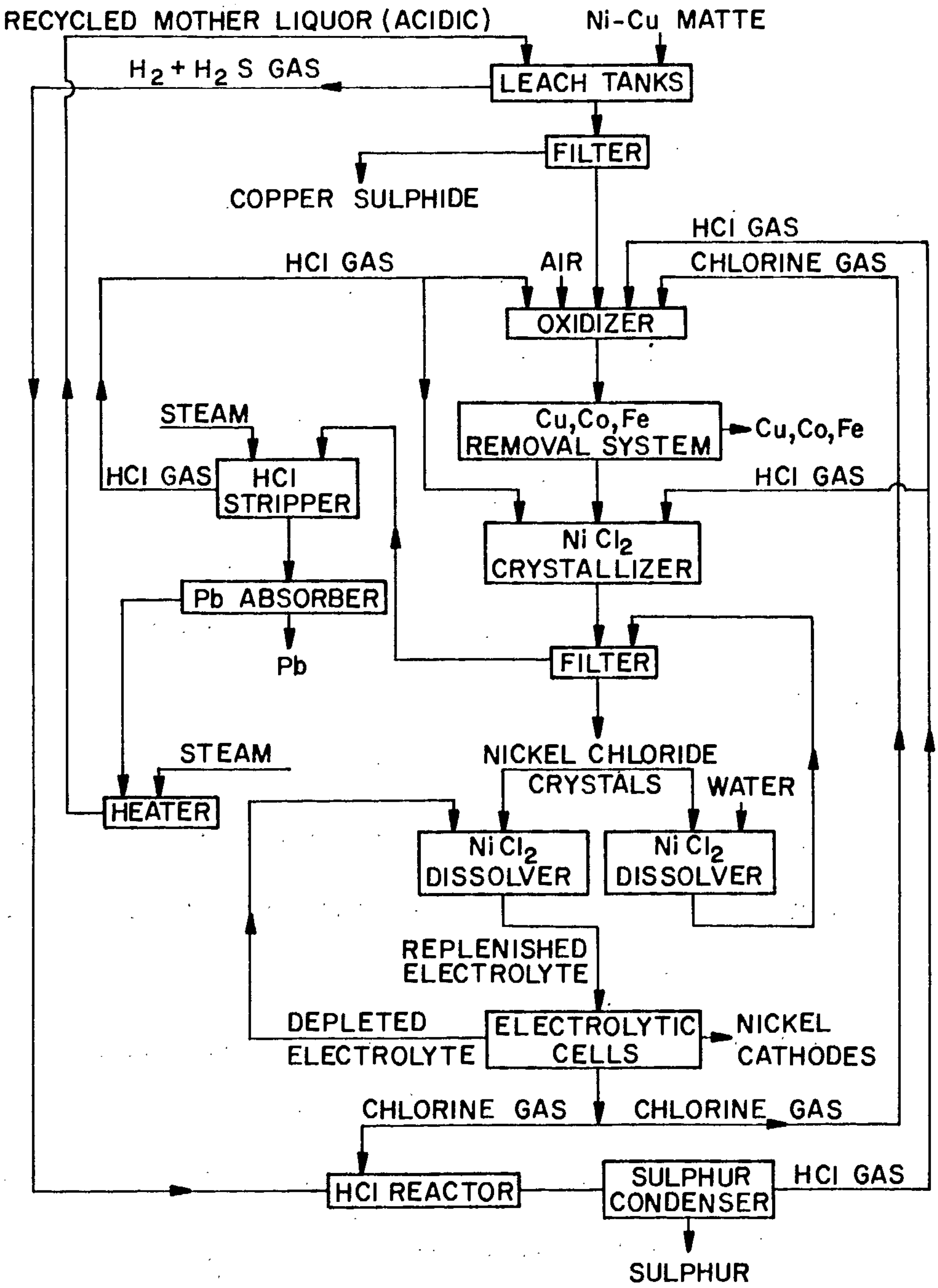


FIGURE 3: Recovery of nickel - Thornhill

mixture of H_2S and H_2 is withdrawn and is reacted with chlorine gas, obtained at a later point in the circuit, to produce elemental sulphur and hydrogen chloride gas. The nickel chloride solution is separated from the copper sulphide residue. The copper, cobalt and iron impurities in the nickel chloride solution are oxidized by the addition of chlorine and hydrogen chloride gas, and removed from solution by means of either ion exchange or solvent extraction. Nickel chloride crystals are obtained from the purified solution, which is then fed back to the leaching tanks. The nickel chloride crystals are redissolved, and the solution fed to an electrolytic cell, where the nickel is recovered as nickel cathodes, and chlorine is evolved for reuse in the circuit. An additional patent(58) discussed the separation of metals, other than nickel, from the metal chloride solution by either ion exchange or solvent extraction methods.

The recovery of iron and sulphur from pyritic-type materials has been the subject of many investigations, and many of the patents and proposed processes describe the generation of H_2S at some stage in the procedure. The general treatment of pyrite was diagrammed by Habashi(59) (Figure 4) in his review of the recovery of elemental sulphur from sulphide ores. This general flowsheet indicates one necessary step when treating pyrite - that of the removal of some of its sulphur content.

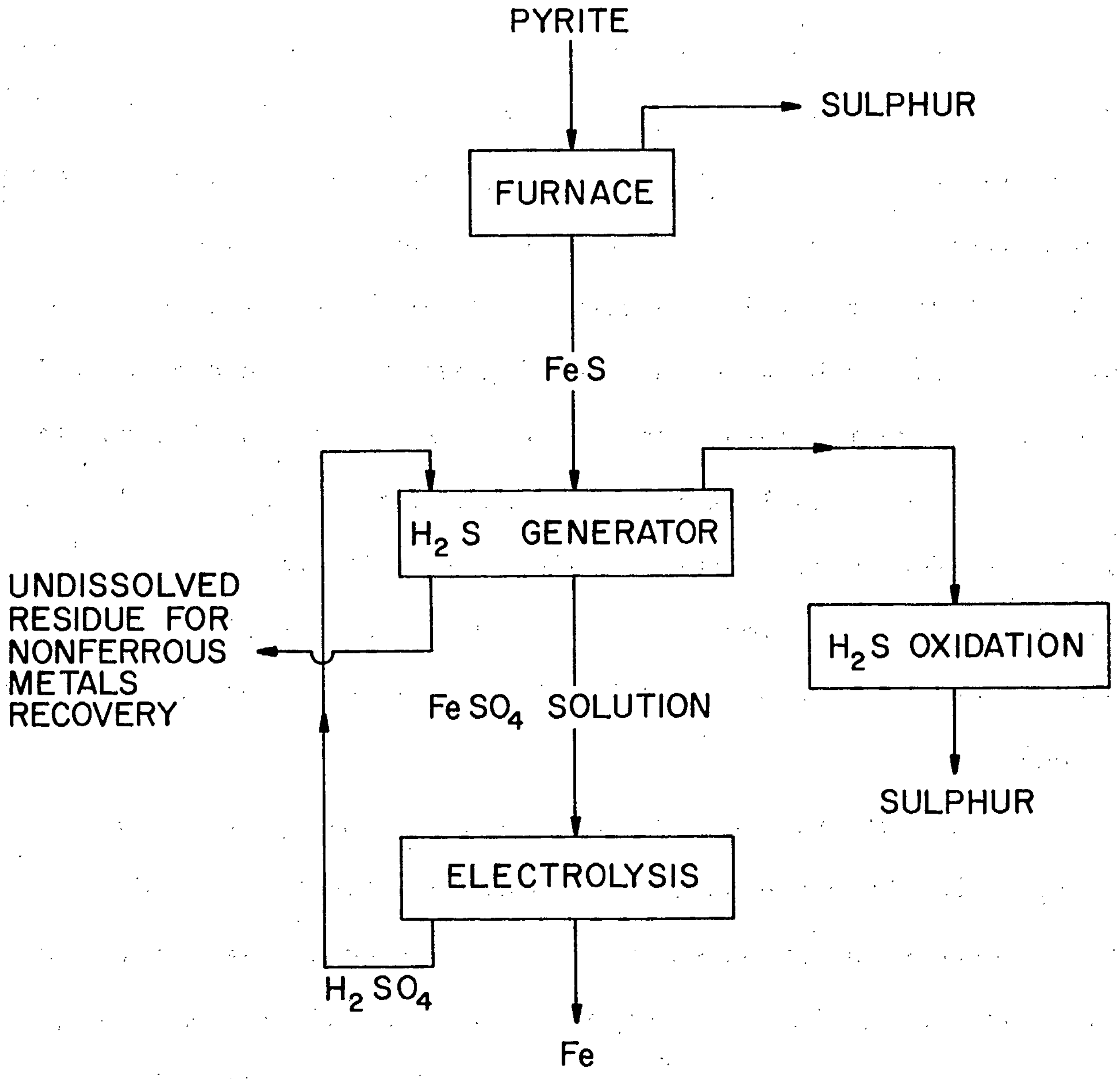


FIGURE 4: Recovery of elemental sulphur from pyrite via H_2S formation - Habashi

The fact that pyrite responds very slowly to treatment by acid has been known for a long time. An early patent on the treatment of pyrite, filed by Estelle(60) in 1915, stated that "..... the excess sulfur is preferably expelled by the application of intense heat with access of air ....". The flow sheet for this patent is shown in Figure 5.

A variety of methods have been used for removing the labile atom of sulphur from pyrite(61). An early patent by Conder(62) (see Figure 6) described the passage of hydrogen over the ores to remove the sulphur prior to leaching. McGauley(63)(64), years later, described a process using hydrogen in a similar manner to desulphurize the ore.

The thermal decomposition of pyrite in a vacuum was studied by Tkachenko, Tseft and Kunseitov(65). They investigated the reaction over the temperature range from 550 to 850°C. Under a pressure of 0.15 mm Hg vacuum, they sublimed off 50 percent of the sulphur, as elemental sulphur, in thirty minutes at 850°C. They leached the residue with boiling HCl (97 g/l) and extracted 99.3% of the iron in two hours. The remaining sulphur was removed as H_2S gas. They concluded that their work demonstrated the feasibility of recovering iron and sulphur from pyrite residues by this treatment.

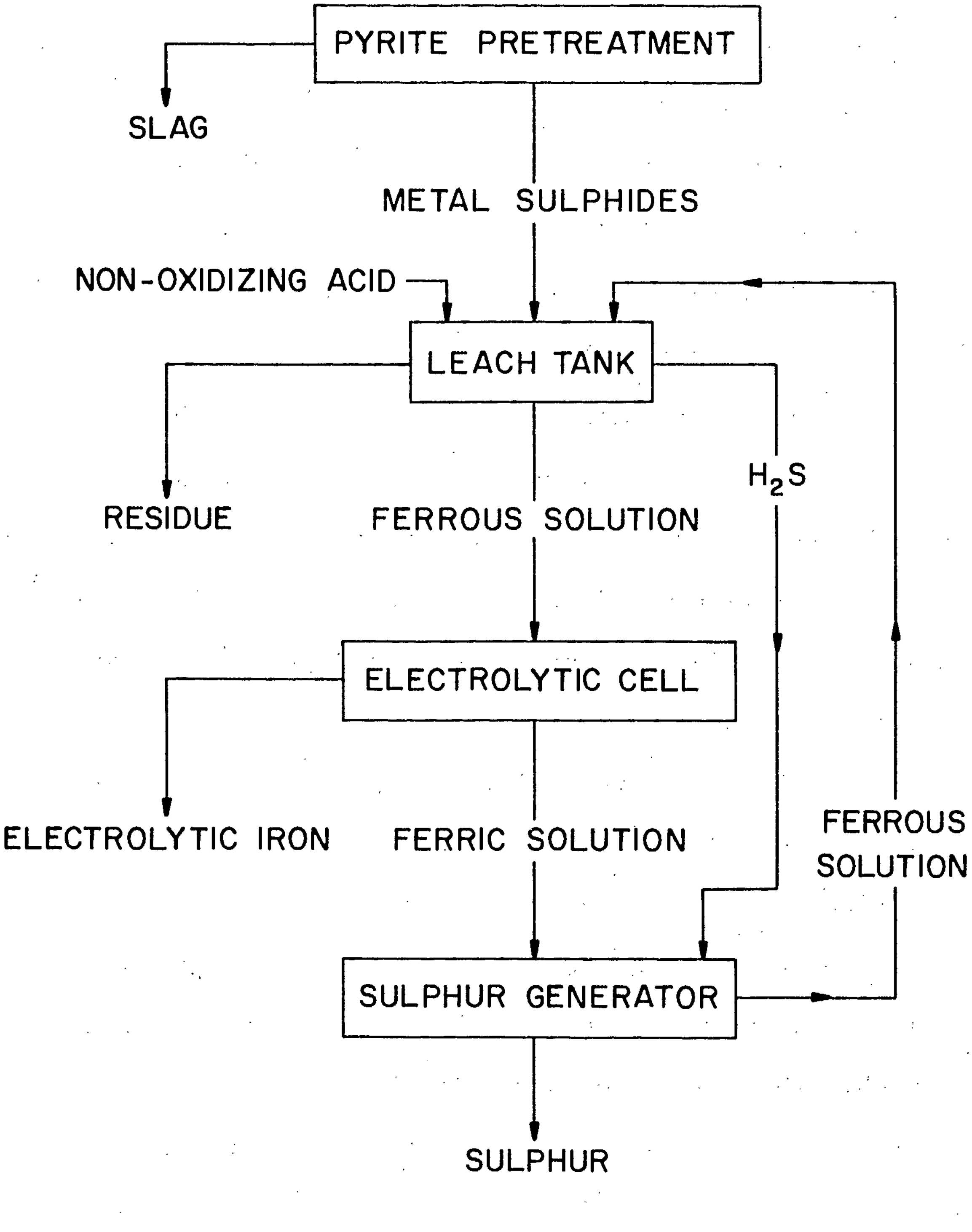


FIGURE 5: Process for treating metallic ores - Estelle

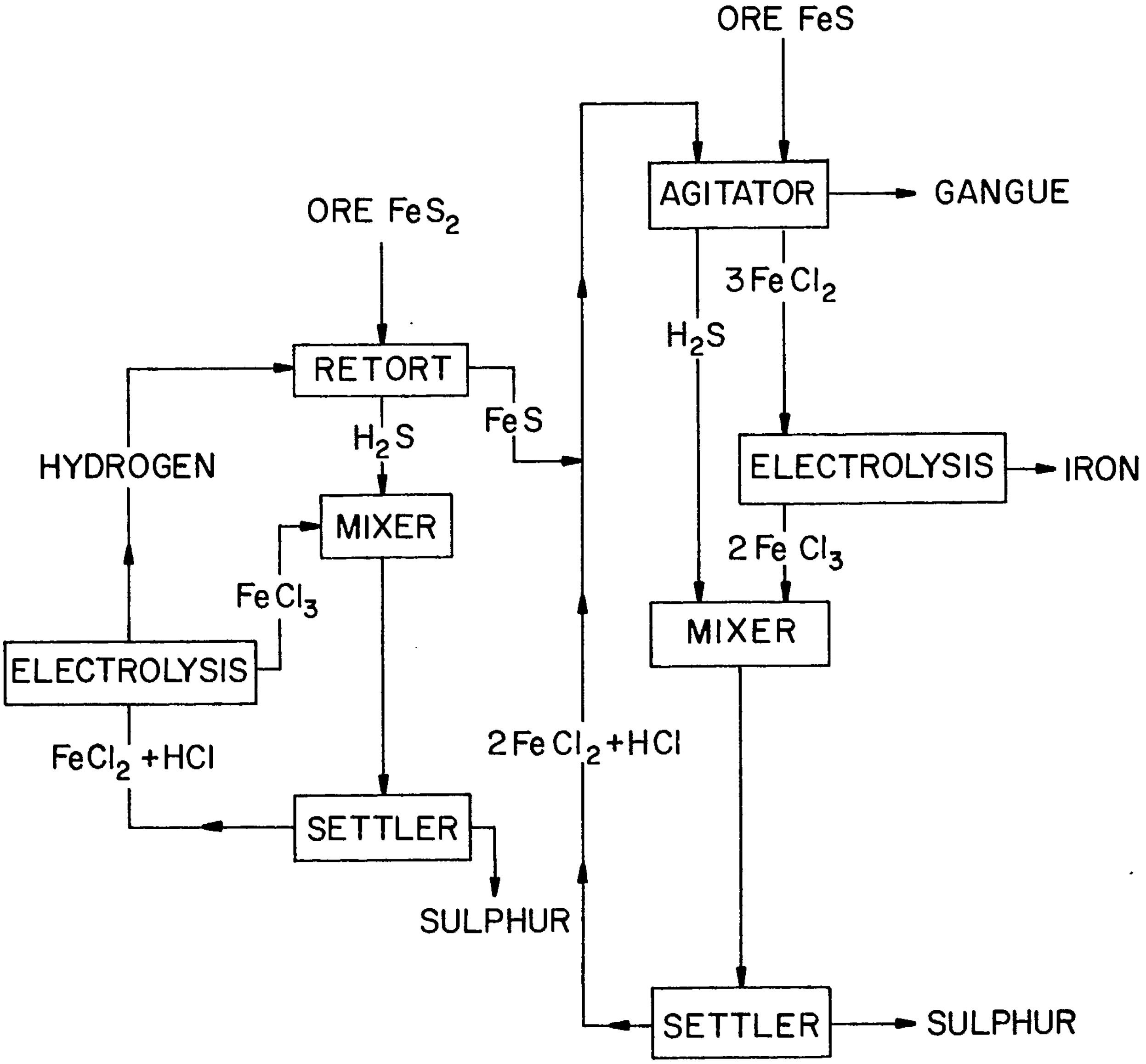


FIGURE 6: Process for recovering iron and sulphur from sulphide ores - Conder

The recovery of labile sulphur from iron pyrites by roasting in the absence of air was investigated by Rajamani and Satyanarayana(66). The variables studied were: ore particle size, retention time, and temperature. Both static roasters and fluidized bed roasters were used. They found that the optimum conditions for achieving the maximum 65 percent recovery of sulphur from a fixed bed were:

Particle size of the ore, 1-2 mm
Roasting period, 20 minutes
Roasting temperature, 650°C

In the fluidized bed, a similar recovery was obtained at 450°C, the other conditions being the same.

Many references describe the roasting of pyrite in the absence of air; the study by Blazek et al.(67) is typical, and the patents by Levy and Gray(68-73) are examples. Several of these described the heating of pyrite in the absence of air at 700-900°C, to obtain sulphur and to prepare a residue that was amenable to acid leaching. Lead was recovered from the leach by electrolysis. The ferrous chloride was converted to Fe_2O_3 by drying and reaction with steam and air(68)(69). In another patent, the mother liquor remaining after removal of the $FeCl_2$ crystals was saturated with

HCl gas and recycled for leaching fresh ore(70). Another patent(71) describes the removal of lead from the solution by precipitation with metallic iron. In another process, the pre-treated pyrite residue was leached with hydrochloric acid, then exposed to air at 60-100°C, before releaching with hydrochloric acid to remove zinc. A copper sulphide concentrate was left as a residue(72)(73).

A typical flowsheet of the treatment of iron sulphide minerals is shown in Figure 7. It is taken from a patent by Bacon(74), who, along with his co-workers, conducted many investigations into the recovery of sulphur from sulphides in the 1930's(74-84). In the process shown in Figure 7, the metallic sulphide was leached with hydrochloric acid in the reaction vat; hydrogen sulphide was produced. The iron was mainly in the ferrous state. The slurry from the reaction vessel was filtered and the solution of ferrous chloride was fed to an evaporator. There, the water and excess hydrogen chloride were driven off and dry ferrous chloride was produced. This ferrous chloride was subjected to the action of steam to produce hydrogen chloride and iron oxide by hydrolysis. The hydrogen chloride and water vapour produced in the process were recycled, and either condensed to form hydrochloric acid or reacted directly with fresh sulphide feed material.

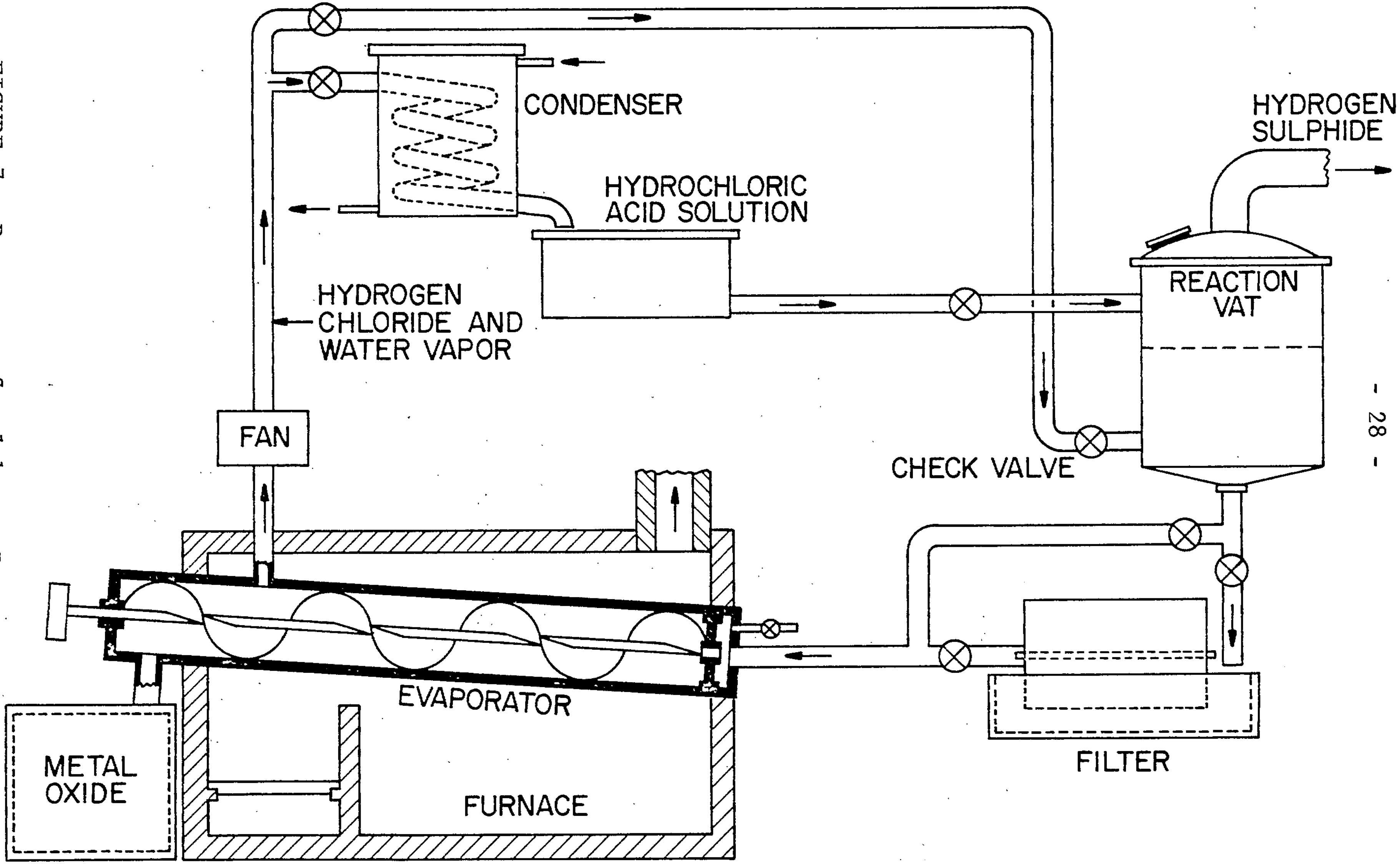


FIGURE 7: Recovery of sulphur - Bacon

Many of the patents filed by Bacon and his co-workers(77-84) involved the treatment of sulphides with hydrogen chloride gas either alone(77), or with air(78), or in the presence of water vapour(79), or in the presence of both water vapour and air(80)(81)(82)(83), or with flue gases, CO_2, CO(86). Two typical flowsheets from Bacon's work are shown in Figure 8 and Figure 9.

In one of Bacon's processes(81) (see Figure 8), ore ground to minus 100 mesh was fed to two separate rotary reactors. The ore passed through these chambers in a direction counter-current to the feed gases. The gas was a mixture of hydrogen chloride, air, and water vapour. The operating temperature of the reactors was 300° to 400°C at the gas-inlet end, and 550° to 600° at the ore-charging end. The products of the reaction were hydrogen sulphide, sulphur dioxide, ferrous chloride, and the chlorides of other metals present in the ore. The metal chlorides were discharged with the unreacted gangue as a solid residue. One reactor was operated under constant conditions of ore feed, temperature, and reagent addition; the other reactor operated under variable conditions such that the gases from the two chambers could be combined in the proper proportions of sulphur dioxide and hydrogen sulphide to produce elemental sulphur according to the reaction:

$$2H_2S + SO_2 \rightleftharpoons 3S + 2H_2O$$

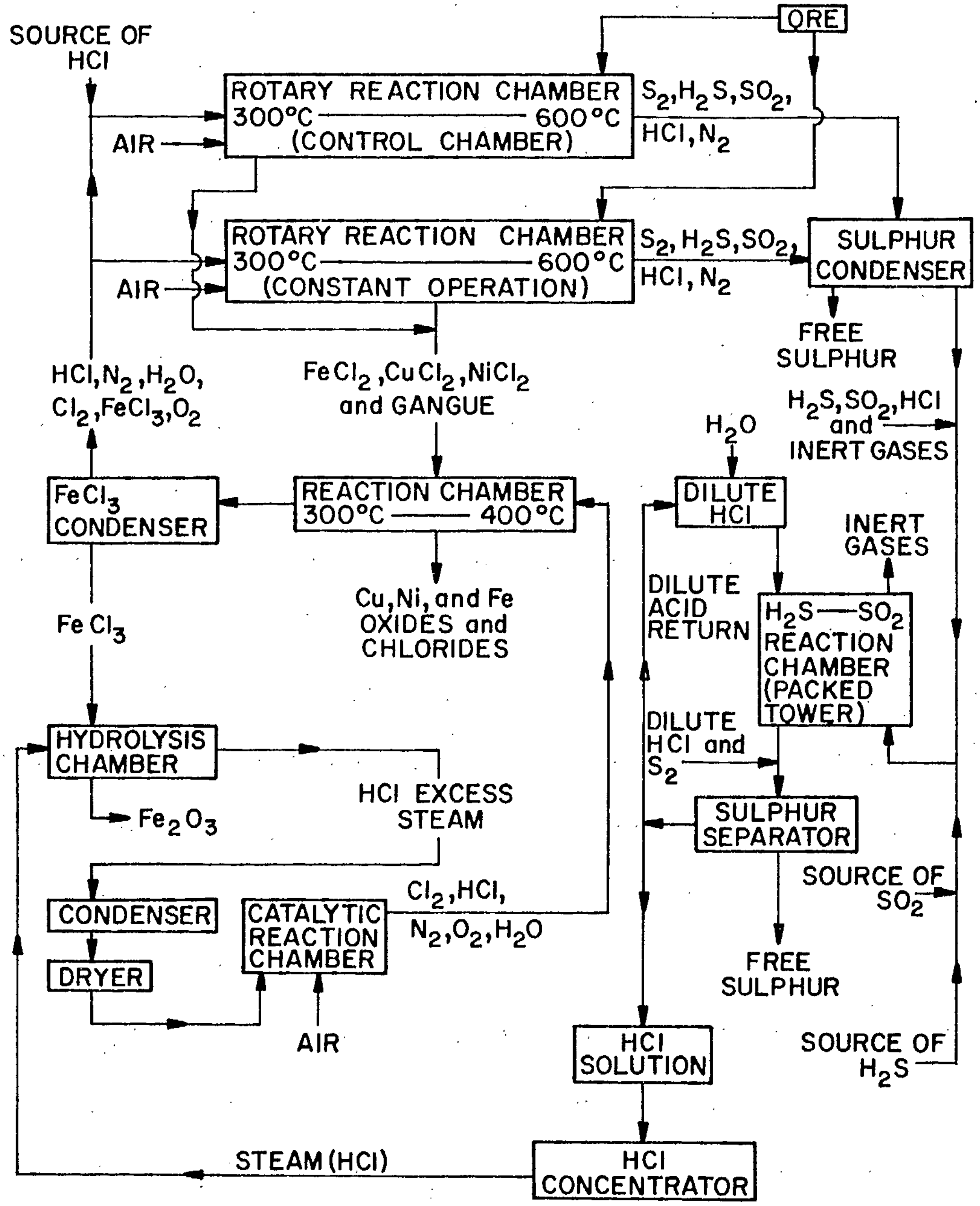


FIGURE 8: Recovery of sulphur - Bacon et al.

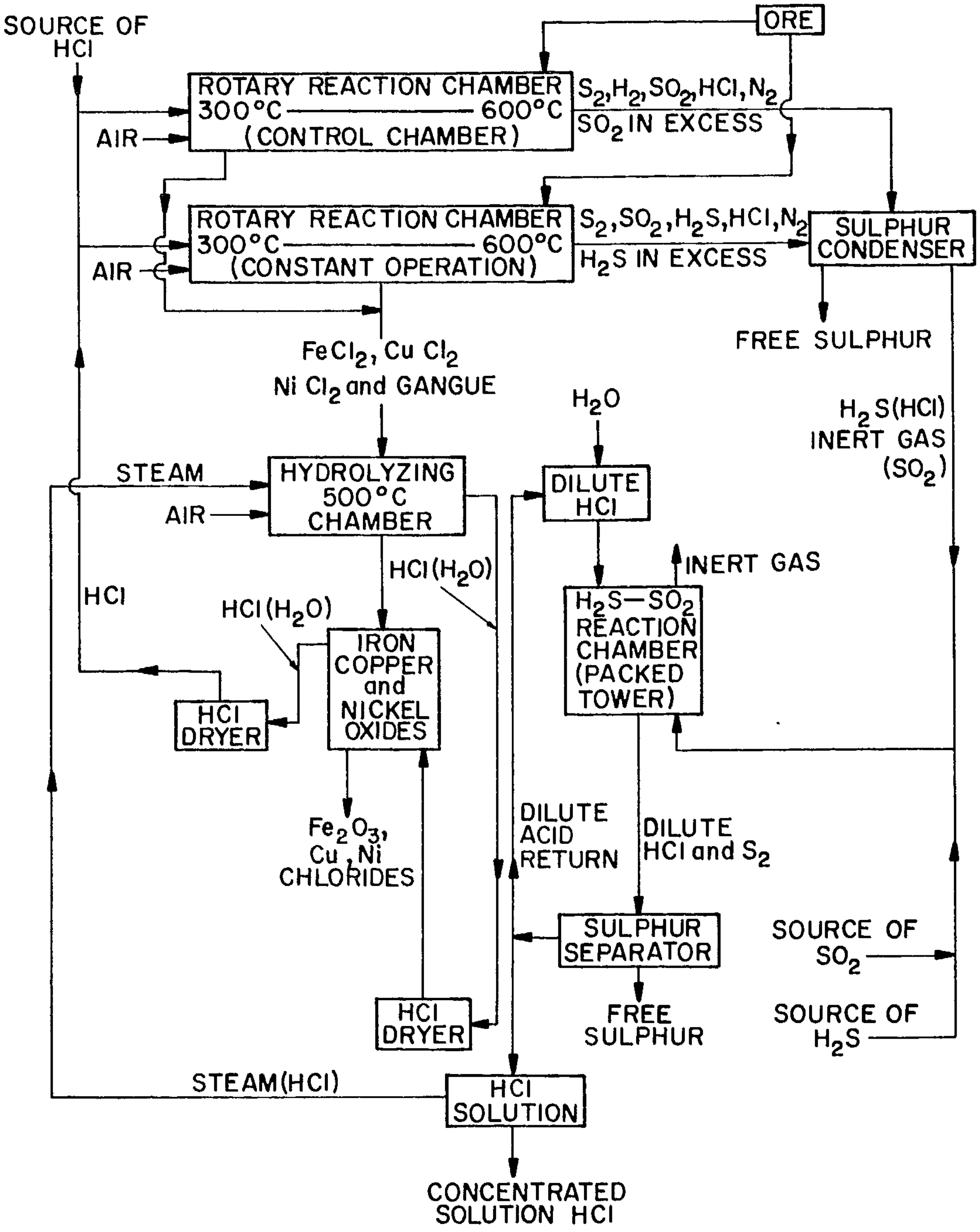


FIGURE 9: Recovery of sulphur - Bacon et al.

In another process(78), illustrated by the flowsheet in Figure 9, the reactor could be operated under conditions that produced an excess of SO_2. It could also be operated to produce an excess of H_2S. The process was controlled to produce two molecules of hydrogen sulphide for every molecule of sulphur dioxide, so as to satisfy the requirements of the above reactions.

An Indian patent(85) describes the treatment of sphalerite ores, with either hydrogen chloride gas or hydrochloric acid, to produce H_2S gas and zinc chloride solution at temperatures from 20 to 40°C. The solution was electrolyzed to produce metallic zinc and chlorine. The chlorine gas was reacted with the H_2S to produce elemental sulphur.

The most recent commercial process utilizing hydrochloric acid leaching is that of Peace River Mining and Smelting, Ltd.(86-89). Although the process was originally developed to treat oxidized iron deposits, it has been observed that it could be applied to the leaching of pyrite or pyrrhotite(88).

Pyrrhotite appears to be the metal sulphide most amenable to the production of hydrogen sulphide. Majima and Peters(3) found that the pyrrhotite reacted in a manner different from the other sulphide minerals they studied. Only pyrrhotite and galena had negative free energies for their reactions with acid to form

H_2S (see Table 1). They noted that pyrrhotite, and to a lesser extent galena, unlike other sulphide minerals, were capable of generating appreciable H_2S pressures at pH values between 2.7 and 11.0. They also commented on the ease with which sulphur was removed from the pyrrhotite crystal as H_2S. Pyrrhotite may possess a high degree of reactivity by virtue of its defect structure.

Maslenitskii and Leonchenkova(90) used modern methods of x-ray crystallographic analysis to prove that the defect structure of pyrrhotite was caused by a solid solution of Fe_2S_3 in FeS. Its formula is generally designated as $Fe_{n-1}S_n$. They showed that although pentlandite did not react with normal HCl solution, pyrrhotite dissolved almost completely after 3 hours at 100°C. Biryukov(91) noted that the solubility of pyrrhotite increased with increasing acidity, and Kunori and Ishii(92) observed the increase in the decomposition of pyrrhotite, and increase of E_h value, with a decrease of pH. Tarabaev and his co-workers(19) also observed the increase in solubility with an increase in temperature, and they found that agitation accelerated the dissolution reaction(93).

Yazawa and Eguchi(94) studied the dissolution of pyrrhotite in sulphuric acid under non-oxidizing conditions, at acid strengths from 0.25 M to 1 M and at temperatures from 30° to

80°C. They followed the progress of the reaction by analysing the solution for its iron content. They conducted their experiments under vigorous agitation to eliminate diffusion control of the reaction. Their results showed that the initial rate of dissolution was directly proportional to the surface area of the suspended pyrrhotite, and that the rate of dissolution was proportional to the H_2SO_4 concentration. They calculated that the activation energy of the reaction was 13.2 kcal/mole.

Achille(95)(96) filed patents in which he described the treatment of pyrrhotite with 20% HCl solution to give H_2S and ferrous chloride solutions. In another patent(97) he described the use of pyrrhotite to react with a solution of sulphuric acid, ferric sulphate and hydrochloric acid which had resulted from a treatment of pyrite with chlorine gas.

An unusual method of treating pyrrhotite was described in patents filed by Takebe(98)(99). These involved the production of hydrogen sulphide from pyrrhotite by electrolysis. The pyrrhotite bed at the bottom of an electrolytic cell was the cathode, and aqueous 5% solution of H_2SO_4 was the electrolyte described in one patent(98), and a 12% solution of H_2SO_4 was the electrolyte described in another patent(99).

KINETICS

General Principles of Leaching

In most leaching processes the reactions that take place are heterogeneous. They are usually of two types: a) most commonly, the reactant in solution reacts with the solid at the surface, and b) more rarely, two substances in solution react with one another (and sometimes with the solid) at the surface of the solid.

Halpern(8), in his discussion of some aspects of the physical chemistry of hydrometallurgy, has summarized as follows the sequence of steps involved in heterogeneous reactions:

1. Absorption of gaseous reactants, if any, by the solution.
2. Transport of dissolved reactants from the main body of the solution to the solid-solution interface.
3. Adsorption of reactants on the solid surface.
4. Reaction on the surface.
5. Desorption of the soluble products from the surface.
6. Transport of the desorbed products into the main body of the solution.

The slowest step in the above sequence determines the rate of the overall process.

The instances in which step 1 is rate-controlling are relatively rare. The effects of pressure, which are pronounced in this step, were discussed by Forward and Halpern(2).

A more common rate-controlling step is that of the transport of materials to and from the reaction site, as in steps 2 and 6. The system is then said to be transport- or diffusion- controlled. The determination of the rate constant is based upon the classical Nernst Theory of Liquid Boundary Layer Diffusion for the rate of solution of solids in aqueous solutions(100). According to this theory, the overall rate of the reaction is controlled by the diffusion of reactants and reaction products through a liquid layer which adheres to the surface of the solid. This liquid layer is composed of molecules or ions that have been formed more rapidly than they could be transported away from the surface. Although this theory has been criticized on the grounds that the hydrodynamics of the system are not adequately represented, and also that many processes are controlled by surface reactions(101,102), nevertheless it is applicable in the majority of leaching reactions.

The generally accepted criteria for diffusion control were listed by Salzberg, Knoetgen, and Molless(103). Two of these criteria are the effect of the stirring rate (through its influence on the boundary layer), an increase of which increases the rate of reaction, and the value of the activation energy, which is low and in the order of 2-7 kcal/mole.

Steps 3, 4 and 5, sometimes grouped together by some authors(2), are not diffusion-controlled, and are referred to variously as "chemical" or "reaction" or "activation" controlled. The criteria for desorption control were listed by Salzberg et al.(103), one of them being the much higher temperature co-efficient, of approximately 25 kcal/mole.

June Zimmerman(104) reviewed the characteristics of chemical and diffusion control of reaction rates. She believes that they represent limiting extremes of behaviour in heterogeneous reactions. She reviewed the temperature coefficient concept for the recognition of a heterogeneous reaction under joint chemical and diffusion-rate control. She also introduced an empirical relationship to illustrate the effect on overall rate of contributions from chemical and diffusional control.

The usefulness of the temperature coefficient as one of the criteria for distinguishing the type of rate control was discussed by Riddiford(105). He showed that an evaluation of the respective contributions of the chemical reaction and transport process to the overall process may be made by use of the temperature coefficient, and discussed the transition from one type of control to another as indicated by a change of slope in the Arrhenius plot.

An example of this change in rate control was shown by Thomas and Ingraham(106) in their investigation of the leaching of covellite. In the temperature range 25° to 60°C, they obtained an activation energy of 22 kcal/mole that is indicative of a chemically controlled process. At 80°C an activation energy of 8 kcal/mole was obtained. This change indicated a shift from chemical to transport control as the temperature increased.

In the chemical- or reaction-controlled, heterogeneous reactions discussed, it has been assumed that the leaching products are entirely soluble in the leaching solution. When a leaching product is insoluble, a layer is formed over the surface. The rate of diffusion of reactants or products through this layer may control the rate of the reaction. Forward and Warren(1) and Pazdnikov(107) discuss this form of rate control by diffusion through coatings of insoluble products on the surfaces of minerals. The dissolution of chalcopyrite(108) is an example of rate control through an insoluble product layer. The system was studied by

Dutrizac et al.(108), who found that the activation energy for the process was approximately 17 kcal/mole. They attributed the parabolic kinetics to the progressive thickening of a sulphur film on the surface of the chalcopyrite.

Peters and Skrivanek(109) had observed that the film theory of mass transfer, commonly used as a model for leaching processes, was poorly supported by the results of experiments in which finely divided material was leached. They therefore developed an alternate model to apply to very fine particles.

They reasoned that when a particle becomes very small the boundary layer becomes very thin, as the forces necessary for its development diminish. For very small particles the film thickness could become larger than the diameter of the particle, and the linear concentration gradient from the particle surface would no longer apply. Finally, the small particles would be inclined to follow the path of the liquid eddy currents.

In developing their model, they made the following assumptions:

1. The surroundings of the particle behave as a non-moving rigid medium through which mass transfer occurs by diffusion.
2. Particles are mono-dispersed and spherical.
3. The volume of soluble particles is negligible compared with the volume of surroundings.

They tested their equation by experimentally leaching uranium ore by a standard sodium-bicarbonate leaching procedure.

They were able to correlate the shape of experimental leaching curves with their mass-transport model. They found that although the model involved the diffusion of solute from the surface of the fine particle as the rate-determining step, the usual dependence of the leaching rate on agitation was absent.

They stated that the most important conclusion that could be drawn from their work was "the absence of an agitation effect when leaching fine particles cannot be relied on as evidence that a mass transport is not rate-determining".

Specific Observations on Sulphides

Several investigations on the solubility of mineral sulphides, and the kinetics of the dissolution in acids, were conducted by Tseft and his co-workers(110-111). In their studies on the solubility rates of zinc and lead sulphide concentrates(110), they used H_2SO_4 (180-200 g/1) at 130°-250°, and HCl (120 g/1) at 80°-220°C, in pressure vessels. Some of the results they obtained were: with H_2SO_4, at temperatures above 200°, in 2 hours, virtually 100% of the Pb, over 60% of the zinc, and less than 20% of the iron. No copper was dissolved from zinc concentrates.

At 100°C, with H_2SO_4, 80% of the lead, 50% of the zinc, about 35% of the iron, but no copper, were dissolved from a lead concentrate. It is interesting to note that the investigators reported that leaching for longer than two hours had little effect. With HCl, above 180°C, over 90% of the lead and zinc were dissolved from the zinc concentrates, and only 25% of the iron. At 100°C, with HCl, 100% of the lead, 55% of the zinc, and 35% of the iron were dissolved from a lead concentrate. From the results of their studies they constructed flow sheets for the selective leaching of zinc, lead, and copper. Separation of the copper was based on the relative insolubility of CuS under the leaching conditions.

In their studies on the kinetics of solution of galena and sphalerite with different solvents, Tseft et al.(111) found that sphalerite dissolved more slowly than galena, and that higher temperatures were needed with sulphuric acid to obtain the equivalent extractions produced by other solvents such as hydrochloric acid.

In their development of a method of extracting zinc from concentrates, Tarabaev, Shchurov and Medvedkov(112) leached the sulphides with a solution containing 152 to 267 g/l $CaCl_2$, 12 g/l HCl, and 200 g/l NaCl. They found that the rate of solution varied with the stirring rate, as is shown by the results in Table 3. We have added a column containing the square root of the stirring speed. From the linearity of the relationship between the time required to dissolve 1.5×10^{-4} mole and the square root of the stirring rate, it is evident that their experiments were done under conditions of rate control by diffusion.

TABLE 3

Time Necessary to Dissolve 1.5×10^{-4} Mole of ZnS

Stirring Rate (rpm)	Time (seconds)	$\sqrt{\text{Rate}}$
240	55	15.5
720	38	26.8
1100	25	33.2

In later studies Tarabaev(93) showed that the decomposition of metal sulphides in stirred HCl solutions was increased by the presence of NaCl. He postulated that the presence of NaCl shifted the following equilibrium to the right:

$$MS + 2H^{+} \rightleftharpoons M^{++} + H_2S,$$

by the formation of NaCl complexes, such as:

$$M^{++} + 3Cl^- \rightleftharpoons MCl_3^-$$

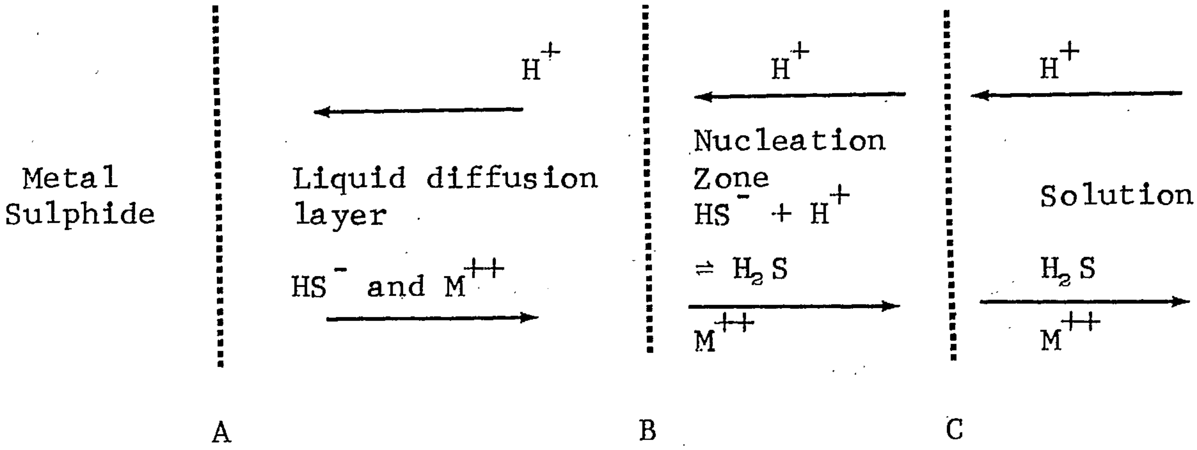
Mechanism of H_2S Release from Sulphides During Leaching

Sufficient information is available now in the literature to permit meaningful speculation on the mechanism of hydrogen sulphide evolution from sulphide minerals immersed in acid solutions. In an excellent analysis of aqueous systems containing ferrous, hydrogen, sulphide and related ions, Pohl(113,114) has shown that the rate of leaching of very finely divided FeS, CdS and ZnS is directly proportional to the concentration of the hydrogen ion. This implies that the rate-controlling reaction involves a single hydrogen ion. The observation would be consistent with the reaction:

$$FeS + H^+ \rightleftharpoons Fe^{++} + HS^- \qquad [5]$$

The suggestion of HS^- as the first product of reaction is also consistent with the potential-pH diagram shown in Figure 1. In it, the range of stability of the HS^- ion extends at 100°C from pH 12 down to about pH 6. Because H^+ is consumed by the above reaction, the only permissible reaction product is one that is stable at low values of H^+. That product would be HS^-.

The experimental work of Tarabaev et al.(93) has shown that the rate of zinc dissolution is diffusion-controlled when the acidity and chloride ion content are held sensibly constant. In addition, the work of Tarabaev(93)(115)(116) has shown that the presence of an excess of chloride ion hastens the rate of dissolution. These observations may be combined to create a general mechanism for the release of H_2S from a sulphide in an acid solution, thus:



The chemical reaction taking place at interface A is normally rapid and is shown in Equation 5. It becomes rate-controlling only when the interfacial area is very large and the diffusion layer is thin. Normally the diffusion of H^+ and HS^- in the layer A-B will be rate-controlling. As the rate of agitation is increased, the thickness of the layer will decrease and the rate of reaction will increase.

In the nucleation zone, B-C, a heterogeneous process occurs. Excess hydrogen ions react with migrating HS^- ions to produce dissolved H_2S, which, when its solubility limit is exceeded, is expelled from the solution. Despite one suggestion by a Russian author(93) there is no strong evidence to suggest that the nucleation and evolution of H_2S is rate-controlling. It is significant, though, that as the concentration of H_2S in the liquid is increased by an over-pressure of H_2S, the rate of dissolution of the sulphide decreases(117)(118). The effect of H_2S over-pressure is obvious from the model. As the pressure is increased, the concentration of HS^- at interface B increases. This causes a decrease in the gradient of HS^- across the layer A-B and decreases the driving force for the transport of HS^- across the A-B layer. Hence, the reaction rate would be expected to decrease.

Because the presence of an excess of chloride ion increases the rate of reaction, it is evident that the rate of diffusion of M^{++} must also be of the same magnitude as that of HS^- and H^+. All three species, HS^-, H^+ and M^{++}, appear to be involved in the diffusional control of the reaction rate.

The postulated mechanism indicates that the rate of metal sulphide dissolution could be increased by:

1. Increasing the interfacial area by fine grinding.
2. Increasing the agitation to decrease the thickness of the diffusion layer.
3. Maintaining a relatively high acidity in the solution.
4. Maintaining a low over-pressure of H_2S.
5. Maintaining a high chloride ion content for promoting ion complexing.
6. When the leaching rate is chemically controlled, the leaching temperature should be as high as is practical. When the rate is diffusion-controlled, very little is to be gained by temperature increases.

CONCLUSIONS

1. Hydrogen sulphide may be produced readily by the reaction of some metallic sulphides with aqueous solutions of hydrogen chloride, with steam and hydrogen chloride, or with slightly moist hydrogen chloride.
2. Pyrrhotite (natural or artifical) appears to have a more rapid reaction rate than many of the other sulphides. As a consequence, selective leaching of the iron is a distinct possibility.

3. When steam or moisture is used with hydrogen chloride, sticking occurs in the temperature range in which the reaction rate is rapid. It is believed that the sticking is caused by low-melting compositions of chlorides and sulphides.

4. When weak aqueous solutions of HCl are used, there is an induction period at the initiation of the reaction. It is not evident when strong (20%) acid solutions are used.

5. The rapid rate of hydrogen sulphide release (and dissolution of pyrrhotite) indicates that a continuous dissolution process might be devised if means were developed for avoiding the induction period in the pyrrhotite reaction. That would permit almost complete utilization of the HCl and would reduce the amount of HCl recycle.

6. The continuous rapid generation of H_2S and the avoidance of sulphur coatings require the exclusion of air or other oxidizing agents during the leach.

7. The choice of acid for liberating H_2S from sulphides favours one that will maintain a non-oxidizing medium, e.g. HCl. The direct generation of sulphur in preference to H_2S involves acids such as H_2SO_4. The economics of recovering acid and iron products from sulphate systems are unfavourable, as indicated in part

by the recent change, from H_2SO_4 to HCl pickling, in the steel industry.

RECOMMENDATIONS

1. Preliminary experiments should be done to establish the nature of the sticking reaction when steam and hydrogen chloride are used to treat mixed sulphides in a fluid bed. If the problem could be resolved, very strong solutions of ferrous chloride could be made during the leach prior to metal ion separations, and the costs of subsequent water evaporation would thus be reduced. (When aqueous hydrogen chloride solutions are used, the concentration of ferrous chloride is determined by the concentration of the acid recoverable by regeneration. This is normally about 20% HCl.) Consideration should also be given to chlorinating the sulphides in a chloride melt.
2. Experiments should be done with the object of determining the nature of the induction period in the pyrrhotite-HCl reaction. The work should be directed to eliminating the induction period and thus permitting the almost complete consumption of acid from a strong ferrous chloride solution. This could lead to the generation of stronger ferrous chloride solutions by HCl gas injection into the leach.

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