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Processes For Sulfur Recovery From Ores

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from Ores

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While the sulfuric acid production is continuously rising, sulfur stocks, on the other hand, are gradually decreasing. It would be, therefore, timely to review the possibilities of sulfur recovery from sources other than brimstone, the primary source for sulfuric acid production. Calcium sulfate deposits (in the form of gypsum or anhydrite), and sulfide ore deposits constitute the most abundant reserve which is not yet extensively exploited as a source of sulfur. The present paper is an attempt to outline the processes known for sulfur recovery from these two sources.

For sulfate ores, thermal, wet, and microbiological methods are discussed. For sulfide ores, pyrometallurgical, hydrometallurgical, and electrolytic methods are outlined. Pyrometallurgical methods involve thermal dissociation, reaction of sulfide ores with \( \text{SO}_2 \) gas, production of sulfur via \( \text{SO}_2 \), reduction smelting, chlorination, and production of sulfur via \( \text{H}_2\text{S} \). Hydrometallurgical methods involve the production of sulfur via \( \text{H}_2\text{S} \), and the aqueous oxidation of sulfide ores. Electrolytic methods involve electrolysis of molten sulfides, and the anodic dissolution of sulfide anodes in aqueous phase.
While sulfuric acid production is continuously rising, sulfur stocks, on the other hand, are gradually decreasing (Table 1). In 1967, U.S. sulfur prices were raised $4.00 per ton and in Mexico $10.00 per ton, making it $32.50 and $50.00 per ton, respectively. World prices run up to $80.00 per ton. Consequently, there has been great interest in studying the possibilities of sulfur recovery from sources other than brimstone. Fig. 1 shows a schematic diagram of sulfur reserves as CaSO$_4$ in anhydrite and gypsum deposits; as FeS, FeS$_2$, PbS, ZnS, etc. in sulfide ore deposits; as H$_2$S (mainly) in natural gas and refinery gas, and as elemental sulfur in brimstone.

This paper is mainly concerned with the first two sources since they are the largest reserves known and, at the same time, the least exploited for sulfur recovery.

Sulfur Recovery from Anhydrite and Gypsum

There are at least three methods known for recovering sulfur from anhydrite and gypsum:

1. Thermal method. Decomposition of anhydrite or gypsum by heating to yield sulfur dioxide according to the reaction:

\[
\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2
\]

requires a high temperature, about 1300°C. The temperature of decomposition, however, can be considerably decreased if the gypsum is mixed with an additive. For example, when coal is added to gypsum, sulfur dioxide can be readily liberated at about 900°C since an intermediate product, CaS, is formed which enhances the decomposition:

\[
\text{CaS} + 4 \text{C} \rightarrow \text{CaS} + 4 \text{CO}
\]

\[
\text{CaS} + 3 \text{CaSO}_4 \rightarrow 4 \text{CaO} + 4 \text{SO}_2
\]

Overall reaction:

\[
\text{CaSO}_4 + \text{C} \rightarrow \text{CaO} + \text{CO} + \text{SO}_2
\]

**Table 1. Sulfur-sulfuric acid balance in U.S.**

<table>
<thead>
<tr>
<th>Location</th>
<th>Year of Construction</th>
<th>Capacity Tons/Year</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leverkusen, Germany</td>
<td>1916</td>
<td>12,000</td>
<td>Experimental later dismantled</td>
</tr>
<tr>
<td>Wolfen, Germany</td>
<td>1938</td>
<td>85,000</td>
<td></td>
</tr>
<tr>
<td>Miramas, France</td>
<td>1937</td>
<td>25,000</td>
<td>Shut down</td>
</tr>
<tr>
<td>Billingham, England</td>
<td>1929</td>
<td>100,000</td>
<td></td>
</tr>
<tr>
<td>Widnes, England</td>
<td>1955</td>
<td>75,000</td>
<td></td>
</tr>
<tr>
<td>Whitehaven, England</td>
<td>1955</td>
<td>150,000</td>
<td></td>
</tr>
<tr>
<td>Breslow, Poland</td>
<td>1950</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>Busko, Poland</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>Zdro, Poland</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>Linz, Austria</td>
<td>1953</td>
<td>50,000</td>
<td></td>
</tr>
</tbody>
</table>

*Preliminary
A process in operation in Europe (Table 2), known as the Müller-Kühne process, is based on this principle. Gypsum, coal, and clay are mixed together and heated in a rotary kiln. Sulfur dioxide formed is used for making acid, while CaO reacts with the clay to form cement—a by-product.

2. Wet method. This method is in commercial operation in many countries (Table 3) and it utilizes gypsum, phosphogypsum (i.e., gypsum produced as a waste product of phosphoric acid manufacture), and anhydrite, instead of sulfuric acid, for making ammonium sulfate fertilizer. Finely ground gypsum reacts at room temperature with an aqueous solution of ammonium carbonate (made by absorbing CO₂ in aqueous ammonia), as follows:

\[(NH_4)_2CO_3 + CaSO_4 \rightarrow CaCO_3 + (NH_4)_2SO_4\]

After filtering off calcium carbonate, the solution is evaporated to crystallize ammonium sulfate which is sold as fertilizer.

3. Microbiological method. This process involves the formation of hydrogen sulfide gas by the action of the reducing bacteria Desulforibrio Desulfuricans on gypsum in the presence of organic matter on which this bacteria lives. The reaction taking place may be represented as follows:

\[\text{Bacteria} \quad \text{CaSO}_4 + C(\text{Organic Matter}) \rightarrow \text{CaS} + 2\text{CO}_2\]

\[\text{CaS} + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{H}_2\text{S}\]

\[\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}\]

Hydrogen sulfide liberated can be collected and converted to elemental sulfur if required, by controlled oxidation:

\[\text{Catalyst} \quad \text{H}_2\text{S} + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{S}\]

In fact, this is the theory advocated by geochemists to interpret the occurrence of sulfur deposits in nature, e.g., in Gulf Coast region. Such deposits are always associated with gypsum, organic matter, and limestone.

SULFUR RECOVERY FROM SULFIDE ORES

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 instance, pure SO₂ was obtained from flue gases by an absorption-desorption process, and in another, 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. 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. Elemental sulfur is easily stored and transported, weighs only one-half an equivalent 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. The following processes are aimed at this goal:

<table>
<thead>
<tr>
<th>Operating company</th>
<th>Date of installation</th>
<th>Raw materials</th>
<th>Annual capacity, tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. BASF (IG Farben Industrie A/G) Oppau, Germany</td>
<td>1913–1914</td>
<td>Gypsum and anhydrite</td>
<td>Up to 500,000 by 1928; later reduced to 110,000</td>
</tr>
<tr>
<td>2. BASF (IG Farben Industrie A/G) Leuna, Germany</td>
<td>1918</td>
<td>Gypsum</td>
<td>Up to 600,000 by 1943; damaged by bombs in 1944; believed rebuilt</td>
</tr>
<tr>
<td>3. Wasag-Chemie Stickstoffwerke Krefeld, Germany</td>
<td>1958</td>
<td>Phosphogypsum</td>
<td>45,000</td>
</tr>
<tr>
<td>4. ICI, Billingham, U.K.</td>
<td>1923</td>
<td>Anhydrite</td>
<td>600,000</td>
</tr>
<tr>
<td>5. ONIA, Toulouse, France</td>
<td>—</td>
<td>Anhydrite</td>
<td>130,000 in 1951</td>
</tr>
<tr>
<td>6. Kuhlman, Selzaete, France</td>
<td>1942</td>
<td>Phosphogypsum</td>
<td>130,000 in 1951</td>
</tr>
<tr>
<td>7. Sindri Fertilizers and Chemicals Sindri, India</td>
<td>1947</td>
<td>Gypsum</td>
<td>200,000 in 1958</td>
</tr>
<tr>
<td>8. Pakistan Industrial Development Daud Khel, Pakistan</td>
<td>1957</td>
<td>Gypsum</td>
<td>300,000</td>
</tr>
<tr>
<td>9. Fertilizers and Chemicals Travancore Limited Kerala, India</td>
<td>1966</td>
<td>Gypsum</td>
<td>100,000</td>
</tr>
<tr>
<td>10. Gujarat State Fertilizers India</td>
<td>Under construction, 1966</td>
<td>Gypsum plus NH₃ and H₂SO₄</td>
<td>50,000</td>
</tr>
<tr>
<td>11. Tohoku Fertilizers Akita, Japan</td>
<td>1956</td>
<td>Phosphogypsum</td>
<td>100,000</td>
</tr>
<tr>
<td>12. OSAG (Österriche Stickstoffwerke) Linz, Austria</td>
<td>1957</td>
<td>Phosphogypsum</td>
<td>33,000</td>
</tr>
<tr>
<td>13. ANIC, Ravenna, Italy</td>
<td>1958</td>
<td>Gypsum</td>
<td>10,000</td>
</tr>
<tr>
<td>14. Azot Sanayii Turkey</td>
<td>Under construction, 1960</td>
<td>Gypsum</td>
<td>45,000</td>
</tr>
</tbody>
</table>

2
Thermal dissociation. To reduce the cost of shipping pyrite, Noranda Co. 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 and the residue is then roasted to $\text{SO}_2$ for sulfuric acid manufacture, i.e.:

$$\text{FeS}_2 \rightarrow \text{FeS} + \text{S}$$
$$2 \text{FeS} + \frac{7}{2} \text{O}_2 \rightarrow \text{Fe}_2\text{O}_4 + 2 \text{SO}_2$$

Outokumpu Oy is operating a plant at Kokkola, Finland, in which pyrite is decomposed in a specially designed furnace at 1800°C by burning fuel oil with preheated air 3-5 percent above the stoichiometric amount. The temperature is high enough to melt FeS formed which can then be easily separated from the sulfur vapor. Residence time in the furnace is only 1.5 seconds. The molten FeS is tapped from the bottom of the chamber, granulated with water and used for making $\text{H}_2\text{SO}_4$ via $\text{SO}_2$.

Pyr;te

**Fig. 2. Recovery of elemental sulfur from pyrite by reaction with $\text{SO}_2$ gas**

Reaction of sulfide ores with $\text{SO}_2$. 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:

$$3 \text{FeS}_2 + 2 \text{SO}_2 \rightarrow \text{Fe}_2\text{O}_4 + 8 \text{S}$$
$$3 \text{FeS} + 2 \text{SO}_2 \rightarrow \text{Fe}_2\text{O}_4 + 5 \text{S}$$

Sulfur dioxide for the reaction can be produced by burning some of the pyrite with air (Fig. 2).

Production of sulfur via $\text{SO}_2$. Sulfur dioxide can be reduced to elemental sulfur by coke, methane, or natural gas at about 1200°C.

(a) Reduction by coke—

The reaction:

$$\text{SO}_2 + \text{C} \rightarrow \text{CO}_2 + \text{S}$$

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

$$\text{CO}_2 + \text{C} \rightarrow 2 \text{CO}$$

to take place, which is endothermic. To achieve the required temperature in the reduction, external heat-

down, the production was 150 tpd of sulfur of 99.9 percent purity.

(b) Reduction by Methane and Natural Gas—

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

$$2 \text{SO}_2 + \text{CH}_4 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + 2 \text{S}$$

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 oxy-
sulfide are formed by side reactions:

$$\text{SO}_2 + \text{CH}_4 \rightarrow \text{H}_2\text{S} + \text{CO} + \text{H}_2\text{O}$$
$$\text{CO} + \text{S} \rightarrow \text{COS}$$
Both can be converted to elemental sulfur by passing the gas mixture over a suitable catalyst at the right temperature. A flowsheet is shown in Fig. 3.

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 Løkken, 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 Rönnskär (Sweden), Mina de S. Domingos (Portugal), Rio Tinto (Spain), and U.S.S.R.

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. 4). Copper is recovered as a molten matte and iron is eliminated 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 SO2. In the middle part of the furnace, the reduction zone, SO2 is reduced by coke to elemental sulfur, which is volatilized as vapor. The reactions taking place can be represented by the following equations:

Upper zone: \[ \text{FeS}_2 \rightarrow \text{FeS} + S \]

Oxidation zone: \[ \text{FeS} + \text{O}_2 \rightarrow \text{FeO} + \text{SO}_2 \]

Middle zone: \[ \text{SO}_2 + \text{C} \rightarrow \text{CO}_2 + S \]

The method has the disadvantage that only copper is recovered; iron and other metals present in pyrite, e.g., cobalt and zinc, are not recovered. The matte produced contains 6-8 percent Cu, is unsuitable for direct converting, and is usually remelted with coke, silica, and limestone to 40 percent Cu.

5. Chlorination of sulfide ores. Chlorine reacts with metal sulfides readily to form metal chlorides and elemental sulfur:

\[ \text{MS} + \text{Cl}_2 \rightarrow \text{MCl}_x + S \]

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 looks promising. The reaction can be conducted in two ways:

(a) Low temperature chlorination at 60-100°C, i.e., at temperatures 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 nonferrous 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, e.g., gold and silver by copper, copper by lead, and lead by zinc. The final solution, containing only zinc, is evaporated under vacuum to anhydrous zinc chloride, which is then electrolyzed in the fused state to metal and chlorine. The cathode is molten zinc and the anode is graphite. The chlorine is collected and reused for the process.

Practically all sulfide ores 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:

\[ 2 \text{FeCl}_2 + 3/2 \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2 \text{Cl}_2 \]

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

\[ \text{CuS} + 2 \text{FeCl}_3 \rightarrow 2 \text{FeCl}_2 + \text{CuCl}_2 + S \]
\[ \text{NiS} + 2 \text{FeCl}_3 \rightarrow 2 \text{FeCl}_2 + \text{NiCl}_2 + S \]

It also reacts with pyrite according to the equation:

\[ \text{FeS}_2 + 2 \text{FeCl}_3 \rightarrow 3 \text{FeCl}_2 + 2 S \]
HYDROMETALLURGICAL METHODS

1. 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:

\[ \text{FeS}_2 + 2H^+ \rightarrow \text{Fe}^{2+} + H_2S \]

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

\[ H_2S + \frac{1}{2}O_2 \rightarrow S + H_2O \]

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. 8 shows a flowsheet of the process.

2. Aqueous oxidation of sulfide ores. Ferric sulfate or ferric chloride solutions dissolve metal sulfides at room
Recovery of elemental sulfur, tin, and zinc from pyrite:

\[
\text{ZnS} + 2 \text{Fe}^{3+} \rightarrow \text{Zn}^{2+} + \text{Fe}^{2+} + \text{S}
\]

The 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, sodium hypochlorite, etc., were used, e.g.:

\[
\text{CuS} + \text{Cl}_2 (aq) \rightarrow \text{Cu}^{2+} + \text{S} + 2 \text{Cl}^{-}
\]

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

\[
\text{ZnS} + 2 \text{H}^+ + \frac{1}{2} \text{O}_2 \rightarrow \text{Zn}^{2+} + \text{S} + \text{H}_2\text{O}
\]

Elemental sulfur is recovered from the residue by pelletizing, melting, and sieving, or by flotation.

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

\[
4 \text{FeS} + 3 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3 + 4 \text{S}
\]

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

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 that the sulfide could 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:

\[
\text{M}^{n+} + 2 \text{e}^- \rightarrow \text{M}
\]

\[
\text{S}^2- + \text{e}^- \rightarrow \text{S}
\]

Overall reaction:

\[
\text{MS} \rightarrow \text{M} + \text{S}
\]

Because the solubility of most sulfides in metal chlorides at 700–800°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:

\[
\text{Na}^+ + \text{e}^- \rightarrow \text{Na}
\]

\[
\text{MS} + 2 \text{Na} \rightarrow \text{M} + 2 \text{Na}^+ + \text{S}^2-
\]

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

\[
\text{MS} + \text{Cl}_2 \rightarrow \text{MCl}_4 + \text{S}
\]

A semi-commercial plant in Wales, recovered lead of 99.95 percent purity and sulfur of 99.5 percent purity from galena by this method.

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°C. A much simpler method is to cast the sulfide in the form of anodes and electrolyze it using an aqueous electrolyte at room temperature. The process can be represented by the equation:

Anodic reaction:

\[
\text{MS} \rightarrow \text{M}^{n+} + \text{S} + 2 \text{e}^- -
\]

Cathodic reaction:

\[
\text{M}^{n+} + 2 \text{e}^- \rightarrow \text{M}
\]
The metal deposits at the cathode, while elemental sulfur remains adhering to the anode in the 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 the form of anodes and recover the metal and the sulfur directly in one step, instead of roasting the matte to oxide, reducing the oxide to metal, and then casting the metal in the form of anodes for electrolytic refining. It should also be noted that this direct electrolysis of sulfide anodes not only bypasses the roasting and reduction step, but it is possible to recover the sulfur directly in the elemental form.

International Nickel Co. of Canada erected a pilot plant in 1951 and a full scale plant at the Thompson refinery in Manitoba in 1964, to apply the process to nickel matte. In this method, nickel sulfide matte is melted at 980°C and cast into anodes. The anodes are allowed to partially cool in the molds 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 anodes corrode smoothly and uniformly, and the sludge formed is granular and porous and adheres 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. The temperature of electrolyte is 55-60°C. The anodes can be electrolyzed to about 10 percent scrap, and the efficiency during the anode dissolution is 95 percent. 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. 9).

White metal, which is mainly Cu₂S, was cast at Montana College of Mineral Science and Technology, Butte, in the form of anodes (fig. 10) and immersed in an acidified CuSO₄ solution containing copper sheet cathode. When an electric current was passed, the anodes were found to corrode smoothly and uniformly, and the slimes formed were granular and porous and remained adhering on the anode (fig. 11). Under the microscope, it was observed that the slimes are composed of two distinct substances: black and yellow particles. These were identified as CuS and elemental sulfur respectively.

The formation of elemental sulfur was found to take place in three distinct steps (fig. 12).

1. During the first three hours, no slimes were formed although copper was continuously deposited on the cathode. During this period, the surface of the anode showed a marked change in color from gray to blue.

2. In the next four hours, elemental sulfur was rapidly formed.

3. After about 10 hours from starting the test, the rate of sulfur formation in the slimes increased slowly but steadily.

Fig. 13. Flowsheet of copper smelting and refining, showing modification whereby white metal can be cast directly from the reverberatory furnace.
Fathi Habashi is associated with the Anaconda Co. as a senior research engineer. Before his service with the company, he was a professor of Metallurgy at the Montana College of Mineral Science and Technology in Butte. Habashi attended the University of Cairo and the University of Technology, Vienna.

After removing the adhering slimes it was found that the residual anode changed its color from gray to dark blue. The change in color was restricted only to a thin layer about one mm thick. This dark blue layer was examined by x-rays and found to correspond to the mineral digenite $\text{Cu}_5\text{S}_4$ (or $\text{Cu}_5\text{S}_4$). The anodic dissolution is believed to take place in three steps:

$$5 \text{Cu}_2\text{S} \rightarrow \text{Cu}_5\text{S}_4 + \text{Cu}^+ + e^-$$
$$\text{Cu}_5\text{S}_4 \rightarrow 4 \text{CuS} + 5 \text{Cu}^+ + S + 5 e^-$$
$$\text{CuS} \rightarrow \text{Cu}^{2+} + S + 2 e^-$$

Spectrographic analysis of cathodic copper was found to be comparable to commercially available electrolytic copper. The process may be applied on commercial scales since it has the advantage of by-passing the converting and poling steps, decreasing pollution problems due to $\text{SO}_2$, and recovering the sulfur of the white metal in the elemental form (fig. 13).

As a result of this work, it was suggested to produce the white metal directly in the reverberatory furnace, i.e., the matte is processed further in the same furnace but in an oxidizing atmosphere and by adding the proper flux till all the iron is removed and the bath attains the chemical composition of white metal. In this way, it would be possible to eliminate the converter completely, and the white metal can be directly cast from the reverberatory furnace.

**CONCLUSIONS**

These are the methods presently known as sulfur recovery from ores. A process can only be successful if it also proves to be economically feasible. This is the challenging question facing the present-day engineers, namely, transforming chemical reactions into technical processes.

**REFERENCES**
