HYPER-ATMOSPHERIC EXTRACTIVE METALLURGY, ITS PAST, PRESENT AND FUTURE

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INTRODUCTION

It is a pleasure and an honour to have been invited to deliver a paper on the rôle of pressure in extractive metallurgy. My objectives will be to review some of the history of this field, its present status and, hopefully, to present some estimate of the future of metallurgical processes under pressure conditions.

It is difficult to know exactly what should be covered here in view of the large number of papers that have been published over the past 10 years. Because of this, I will devote a substantial portion of this report to areas of possible interest that have not previously been fully discussed.

Aqueous solution leaching at elevated temperatures and pressures is one of the most significant technological developments in extractive metallurgy in recent years. There are few ores, concentrates, metals or alloys that cannot be placed in solution when the correct conditions are present. This very fact has caused those of us using pressure leaching systems some consternation from time to time. This technique is characterized by high reaction rates and, consequently, large capacities per operating unit. The reason for this is the fact that the concentration of the gaseous reactants, i.e. oxygen or hydrogen, and temperature, can be increased to levels far above those attainable at atmospheric pressures.

If extractive metallurgy under pressure conditions has a beginning point, it must have been during the cooling of the mass we know as earth. Here, hydrothermal processes have been in progress for eons and certainly many of the recoverable metal values we depend on today are the result of pressure and temperature concentration processes. Mother Nature has skillfully applied this science and today there are a number of naturally occurring minerals we cannot as yet synthesize in the laboratory.

Two of man’s most spectacular achievements in this vein are the hydrothermal growth of quartz single crystals by Bell Telephone Laboratories and the high temperature–high pressure synthesis of diamond by General Electric Company.

We find many examples in which an idea or a concept has been developed and used long before its obvious extension to directly related fields. In a rather direct sense, this situation existed in the application of pressure to extractive metallurgy. It is somewhat amazing that the general concept of the Bayer Process was not applied to other areas of extractive metallurgy until some 60 years after its invention by Bayer of Germany in 1888. This process is man’s earliest successful example of pressurized high temperature
leaching in aqueous solutions. Here, caustic soda solutions at temperatures of 160–170° are used for the dissolution of bauxite without oxidation.

Aqueous solution reduction processes for metallic salts were likewise known for almost 100 years, according to Schaufelberger, prior to its successful industrial application.

Of the early investigators in this field, Ipatiev was most notable. His work started in 1906 with an investigation of the effect of hydrogen on the reduction of nickel oxides. This was followed by a series of five papers on the deposition of metals from aqueous solutions of their salts by hydrogen at high temperatures and pressures. Ipatiev's investigations included many metals (platinum, iridium, copper, nickel, cobalt, lead, tin, arsenic, antimony, bismuth) under rather extreme pressure and temperature conditions. Unfortunately, the effect of pressure was possibly over-emphasized with little attention to buffering of the solutions to prevent basic salt precipitation.

The first application of high pressure aqueous solution leaching of sulphide minerals using oxygen, is described in a German Patent by Henglein and Neimann early in 1927. This patent describes the autoclave aqueous solution leaching of zinc sulphide at 180° with an oxygen overpressure of 20 atmospheres. Complete conversion to the sulphate was obtained in 6 hours. This patent discloses the basic concepts on which the current pressure leaching technology is based.

Early in 1952, the metallurgical fraternity was excited and, to a degree, alarmed, by the announcement of the new pressure leaching and hydrogen reduction process developed by the Chemical Construction Company, then a subsidiary of American Cyanamid Company. The new process was described in optimistic terms by Major General William N. Porter, then President of Chemetals.

General Porter portrayed the Chemico process as "New process, completely chemical; may cut the cost of producing such strategic metals as cobalt, nickel and copper by more than half. The process bypasses roasting, smelting, electrolytic and fire refining.—Limitless opportunity for the process."

This optimism was justified in view of remarkable leaching rates, efficiency of extraction and apparent simplicity of handling complex ores. It is my firm belief, however, that this rather unrealistic appraisal delayed the development of the ultimate capabilities of this process.

At the time of the announcement of the Chemico Process, it was revealed that three plants which would use this method were under construction. Sherritt Gordon Mines Ltd in Canada would use Forward's ammonia pressure leaching system for the extraction of nickel, copper and cobalt from Lynn Lake concentrates. The National Lead Company in Fredricktown, Missouri, selected acid pressure leaching to extract nickel, cobalt and copper from complex sulphide concentrates. The Calera Mining Company at Garfield, Utah, would also use acid leaching for the extraction of cobalt from arsenical concentrates.

Of these three, the Calera Mining Company, a subsidiary of the Howe Sound Company, would have the dubious honour of being first on stream.
in the fall of 1952. The problems of start-up of this plant were formidable. Two basic problems were largely responsible for these difficulties. First, the abrasive nature of sulph-arsenide concentrates on the high pressure slurry pumps required to feed the autoclave. Second, the fantastic corrosive and abrasive nature of the acid autoclave solutions on all parts of the pressurized system. While some corrosion had been experienced in the tests at the Linden Laboratory of Chemico, the problems were orders of magnitude greater on the full plant scale.

It should be remembered that at the time the Calera Plant was designed, built and placed on stream, no pilot plant work had been done on the acid process. Many of the materials of construction that were ultimately to prove successful in the corrosive environment were in the research and development stage; application techniques for these new materials were yet to be devised; the chemistry of the process was quite unknown; and suitable pumps for high pressure delivery of the abrasive concentrate slurries at low flow rates were yet to be invented. Thus, the plant became a proving ground for materials, application techniques, specialized high pressure equipment, and for the engineers of Calera Mining Company and the Chemical Construction Company responsible for the solution of these problems.

HISTORY OF THE CALERA REFINERY

Because of economic failure, the Calera Refinery has become only history. High operating costs made it impossible to compete in the world market. Relatively little has been published on the Calera Plant, and since it represented the first acid leaching process operating on arsenical ores, I will touch on a few interesting aspects of this operation.

The Calera concentrate, produced at the Blackbird Mine some 40 miles west of Salmon, Idaho, consisted of a mixture of cobaltite (CoAsS) and pyrite (FeS₂) with varying small percentages of gersdorffite (NiAsS), chalcopyrite (CuFeS₂) and arsenopyrite (FeAsS). The gangue minerals were mica, quartz and chlorite. The cobalt grade would vary depending on the nature of the ore—the oxidized zones being appreciably more difficult to concentrate. In general, the average cobalt grade was near 17.5 per cent with 20 per cent iron, 24 per cent arsenic, 29 per cent sulphur, 1 per cent nickel and 1.5 per cent copper.

The flow sheet of the Calera Refinery as originally designed is shown in Figure 1.

After approximately a year of difficulties, Chemico agreed to undertake the responsibility for plant modifications required to reach the designed production rate. During this period, substantial progress was made and in December of 1955, Calera management resumed operation.

Process and mechanical developments were contributed by Calera during the next two years to further reduce operating costs. The final flow sheet is shown in Figure 2. The problem areas and best solutions available in 1959 are summarized in Table 1.

The chemistry of the acid pressure leaching of the sulph-arsenide type concentrates represents an interesting system of simultaneous and consecutive
Figure 1. Calera Refinery flow sheet—1/1953
<table>
<thead>
<tr>
<th>Plant location</th>
<th>Materials used</th>
<th>Corrosion environment and remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate mixing system and transfer lines</td>
<td>Type 316 stainless steel agitators and piping; rubber lined concentrate slurry storage tanks</td>
<td>Slurred Cobaltite concentrates; pH 2.0-4.0 at atmospheric pressure and temperature</td>
</tr>
<tr>
<td>Centrifugal pumps for feed to high pressure pumps</td>
<td>Rubber lined; steel with Type 316 or rubber covered impellers</td>
<td></td>
</tr>
<tr>
<td>High pressure automatic air displacement feed pumps and piping to leach autoclave</td>
<td>Case—rubber lined steel</td>
<td>600–625 p.s.i. concentrate slurries at ambient temperature</td>
</tr>
<tr>
<td></td>
<td>Check valve system—Stainless steel</td>
<td>600–625 p.s.i. concentrate slurries from ambient to 400–475°F</td>
</tr>
<tr>
<td></td>
<td>Ballcheck with rubber seats</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low frequency operation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Titanium (unalloyed) piping to leach autoclave</td>
<td></td>
</tr>
<tr>
<td>Autoclave—lining</td>
<td>Type 316 stainless steel clad, steel pressure vessel with 2–4 in. layers of Pb lining and 4–6 in. acid proof brickset with potassium base mortar</td>
<td>Reacting concentrate slurry at 575–600 p.s.i. total pressure at 875 to 475°F with Ca^{2+}; 0–60 g/l; Fe^{3+}; 0–60 g/l; Fe^{2+}; 0–100 g/l; H_{2}SO_{4}; 0–200 g/l; As^{3+}, As^{5+}, Fe AsO_{4} and gangue minerals</td>
</tr>
<tr>
<td>Compartment separations</td>
<td>Carbon brick set with National Carbon C-6 cement</td>
<td></td>
</tr>
<tr>
<td>Agitators</td>
<td>All-welded titanium</td>
<td></td>
</tr>
<tr>
<td>Agitator shafts</td>
<td>Titanium to packing gland; Carpenter 20 and similar alloys through packing gland; bearing surfaces metalized with high Cr alloys; all exposed parts protected with Ti shroud</td>
<td></td>
</tr>
<tr>
<td>Let down system 575–600 p.s.i. to 1 atm</td>
<td>All piping titanium; gas and steam let down; alumina choke set in Type 316 stainless with Pb–Sn–Sb alloy KT grade silicon carbide throttling disk set with Pb–Sn–Sb alloy</td>
<td>Very high velocity gas at 450–550°F with acid mist, some solids, Fe^{3+}, Fe^{2+}, etc.</td>
</tr>
<tr>
<td>Slurry let-down system 575–600 p.s.i. to 1 atm</td>
<td>All piping titanium; long conical taper machined from Ti bar; stock to chock section flow controlled with 6 in. to 8 in. bore KT grade silicon carbide choke set with Pb–Sn–Sb alloy</td>
<td>Discharge to atmospheric pressure</td>
</tr>
<tr>
<td>Autoclave feed of lime purification residue to 5th autoclave compartment</td>
<td>Same pump design and construction as high pressure autoclave concentrate feed pumps</td>
<td></td>
</tr>
</tbody>
</table>
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reactions. Some idea of the chemistry involved can be obtained from the following series of reactions:

\[ 4 \text{FeS}_2 + 15 \text{O}_2 + 2 \text{H}_2\text{O} = 2 \text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{SO}_4 \] \hspace{1cm} (1)

\[ 4 \text{CoAsS} + 13 \text{O}_2 + 6 \text{H}_2\text{O} + 2 \text{Fe}_2(\text{SO}_4)_3 = 4 \text{CoSO}_4 + 4 \text{FeAsO}_4 + 6 \text{H}_2\text{SO}_4 \] \hspace{1cm} (2)

\[ 4 \text{NiAsS} + 13 \text{O}_2 + 6 \text{H}_2\text{O} + 2 \text{Fe}_2(\text{SO}_4)_3 = 4 \text{NiSO}_4 + 4 \text{FeAsO}_4 + 6 \text{H}_2\text{SO}_4 \] \hspace{1cm} (3)

\[ 2 \text{FeAsS} + 7 \text{O}_2 + 2 \text{H}_2\text{O} = 2 \text{FeAsO}_4 + 2 \text{H}_2\text{SO}_4 \] \hspace{1cm} (4)

\[ \text{CuFeS}_2 + 4 \text{O}_2 = \text{CuSO}_4 + \text{FeSO}_4 \] \hspace{1cm} (5)

\[ 2 \text{FeSO}_4 + \text{H}_2\text{SO}_4 + \frac{1}{2} \text{O}_2 = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \] \hspace{1cm} (6)

\[ \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 = 2 \text{FeH}(\text{SO}_4)_2 \] \hspace{1cm} (7)

These reactions are not intended to indicate the sequence involved. However, they were useful in calculations of the arsenic-to-iron ratio, yield of sulphuric acid, and over-all energy of the reaction for various grades of cobaltite concentrate. These three factors, adjustable by blending concentrates, were essential in maintaining acceptable autoclave chemistry and filterable pregnant cobalt sulphate slurries.

The over-all process can be represented by the equation

\[ \text{CoAsS} + \text{FeS}_2 + \text{NiAsS} + \text{CuFeS}_2 \xrightarrow{\text{O}_2, \text{H}_2\text{O}} \text{CoSO}_4 + \text{NiSO}_4 + \text{CuSO}_4 + \text{FeSO}_4 + \text{FeAsO}_4 + \text{FeH}(\text{SO}_4)_2 \]

The gangue minerals, mica and chlorite, were dissolved, while the silica was probably converted to silicic acid gels. This may have been responsible for the non-filterable nature of leached slurries from low grade concentrates (12-14 per cent Co).

Of the products from the autoclave, only the identification of FeAsO_4 and FeH(SO_4)_2 was a problem. Detailed X-ray diffraction and chemical analysis studies proved that the arsenic was made insoluble as the anhydrous ferric arsenate. Significantly, the ferric arsenate was formed in preference to cobalt, nickel or copper arsenates under autoclave conditions. This would not be expected from available solubility data. The FeH(SO_4)_2 represented more of a problem. This compound was shown by X-ray diffraction to be isomorphous with FeSO_4. It may be synthesized by autoclave oxidation of ferrous sulphate solutions containing 60 to 100 g/l of free sulphuric acid at 400°F with at least 50 p.s.i.a. oxygen overpressure. It is pale yellow in colour and extremely insoluble. The formation of this compound enhanced the neutralizing power of the lime purification residue returned to the fifth autoclave compartment as shown in Figures 1 and 2.

Under ideal conditions, the concentration of Fe^{2+}, Fe^{3+}, As^{3+} and As^{5+} could be reduced to very low levels in the autoclave end process liquors. The general course of these reactions is shown in Figure 3.

Under normal operating conditions, all the sulphur was ultimately converted to sulphate or sulphuric acid. The formation of insoluble ferric
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Arsenate liberated additional sulphuric acid essential for leaching CoAsS and eliminated the arsenic disposal problem.

![Graph showing concentration of metal ions vs. time](image)

*Figure 3. Metal ion concentration v. leaching time—cobaltite concentrate*

Pyrite, the principal secondary mineral in the Calera cobaltite concentrates, proved to be an extremely important constituent in the successful leaching of arsenical ores. Cobaltite, in the absence of strong sulphuric acid is inert under autoclave conditions. With sulphuric acid at a concentration of 100 g/l, the reaction will proceed, but the pregnant liquors contain large quantities of arsenic acids that apparently polymerize, forming a gel, resulting in non-filterable slurries. Thus, a workable acid pressure leaching system for arsenical ore depended on a controlled balance of arsenic, iron and free sulphuric acid. The same conditions were found necessary for other arsenides such as CoAs₂, NiAs₂, and cobaltian speisses.

Because of the importance of iron and sulphuric acid in the leaching of arsenical ores, the mechanism of leaching of pyrite, investigated by McKay and Halpern, is significant. Their results suggest that two reactions are principally responsible for the leaching of ferrous sulphide, namely:

\[
\text{FeS}_2 + 2\text{O}_2 \rightarrow \text{FeSO}_4 + \text{S} \tag{8}
\]

\[
2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{FeSO}_4 + 2 \text{H}_2\text{SO}_4 \tag{9}
\]

This is in general agreement with the observations at Calera. At low autoclave temperatures, elemental sulphur was formed by the reaction suggested in equation (8). This resulted in the formation of sulphur-bonded pyrite "balls" ranging in size from "bird shot" to massive encrustations and boulders over a foot in thickness. Needless to say, the life expectancy of the titanium agitators was short under such conditions. Once sulphur-bonded materials were formed, they could not be chemically removed even with the higher autoclave temperatures normally used.

Laboratory experiments confirmed the fact that elemental sulphur was unreactive under autoclave conditions (i.e. 350–450°F at 50 to 100 p.s.i. O₂ in 50 g/l. H₂SO₄ solutions). In the light of these results and in the absence
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of elemental sulphur in the autoclave slurry discharge under normal operating conditions, the mechanisms of reaction proposed by McKay and Halpern does not seem directly applicable to the high acid systems. Their proposed mechanism suggests that ferrous sulphate and sulphur are formed in equimolar ratios from the oxidation of ferrous sulphide. Further work is needed to clarify this point.

In spite of the work done on the leaching of cobaltite, the exact mechanism of dissolution remains obscure. As mentioned above, the reaction

\[ 4 \text{CoAsS} + 13 \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 4 \text{CoSO}_4 + 4 \text{H}_3\text{AsO}_4 \]

will not proceed at a usable rate even at 450°F and 150 p.s.i. O\textsubscript{2} overpressure in the absence of sulphuric acid. It was found that the rate of extraction of cobalt increased directly with the sulphuric acid concentration of the slurry up to 100 g/l. As an example of this effect, if the initial sulphuric acid concentration in the slurry was 100 g/l., over 90 per cent of the cobalt would be converted to cobaltous sulphate in 5 minutes at 425°F and 50 p.s.i. O\textsubscript{2} overpressure. This fact suggests that adsorption of undissociated sulphuric acid on the CoAsS surface may be involved in the dissolution. In some respects, the reaction may be quite like the dissolution mechanism recently proposed\textsuperscript{9} for nickel.

PRESENT STATUS OF HYPER-ATMOSPHERIC EXTRACTIVE METALLURGY

The past ten years of extensive laboratory research, pilot plant development and plant scale operation have proved the technical feasibility of pressure leaching and hydrogen reduction. Unfortunately, the economic status of the process is less clearly defined. Many of the production facilities have been partially dependent on economic concessions of some type.

Since this technique represented an entirely new concept of hydrometallurgy, the initial plant costs were high. The specialized equipment involved and the new designs required to perform the unit operations resulted in disproportionately high engineering and development costs. This is particularly true when compared to conventional pyro-, hydro- and electrometallurgical processes.

Likewise, many of the materials of construction required were new, scarce and expensive in the early phases of industrial development. Titanium, for example, an absolute necessity in the acid leaching process, ranged in price from $50 to $150/lb. in fabricated shapes in 1952. Today, this metal is almost competitive with type 316 stainless steel.

All of the operating plants using the Chemico Process have been described in recent metallurgical literature. Therefore, I will only summarize in Table 2 some of the pertinent details for comparison in terms of acid, ammoniacal or basic autoclave leach conditions.

A number of laboratory, and in some cases, pilot plant, investigations have been conducted that suggest other areas of application. Their future development, however, depends predominantly on economics\textsuperscript{20–26}.
### Table 2. Summary of processes and current status

<table>
<thead>
<tr>
<th>Company</th>
<th>Concentrate</th>
<th>Pressure leach conditions</th>
<th>Hydrogen reduction conditions</th>
<th>Products</th>
<th>Current rate of production</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acid leach</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>National Lead Company</td>
<td>Complex Cu, Ni, Co sulphide (Siegenite)</td>
<td>373-474°F @ 600 p.s.i.g. air</td>
<td>375°F @ 750-800 p.s.i.g. H₂</td>
<td>Ni briquettes</td>
<td>Closed—political</td>
<td>10</td>
</tr>
<tr>
<td>Freeport Sulfur Co.</td>
<td>Laterite</td>
<td>475°F @ 525 p.s.i. 650 p.s.i. steam + 98% H₂SO₄</td>
<td>Ni 375°F @ 750 p.s.i. Co—unpublished</td>
<td>Co briquettes (NH₄)₂SO₄</td>
<td>Closed—economic</td>
<td>11</td>
</tr>
<tr>
<td>Calera Mining Company</td>
<td>Cobaltite</td>
<td>375-475°F @ 600 p.s.i.g. air</td>
<td>375°F @ 750-800 p.s.i.g. H₂ (electrolytic)</td>
<td>Co + Ni powder</td>
<td>Decision reached to install acid circuit for ores not amenable to ammoniacal leach</td>
<td>12</td>
</tr>
<tr>
<td>Sherritt Gordon Mines Ltd</td>
<td>Cobalt and nickel conc.</td>
<td>Probably similar to Calera</td>
<td></td>
<td>Ni—Co—</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>Whitaker Metal Co. Fluor Corp.</td>
<td>Copper base scrap</td>
<td></td>
<td></td>
<td></td>
<td>?240,000 lb. Cu/mo.</td>
<td>2</td>
</tr>
<tr>
<td><strong>Ammoniacal leach</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sherritt Gordon Mines Ltd</td>
<td>Ni, Cu, Co, Fe sulphide conc.</td>
<td>(1) 170–200°F @ 100–150 p.s.i.g. air</td>
<td>375°F @ 750–800 p.s.i.g. H₂</td>
<td>Ni powders and briquettes</td>
<td>Ni—23,258,000 lb./year</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) Thionate oxidation 350–400°F @ 700–800 p.s.i.g. air</td>
<td></td>
<td>Co powders and briquettes (NH₄)₂SO₄</td>
<td>Co—310,000 lb./year</td>
<td>14</td>
</tr>
<tr>
<td><strong>Basic leach</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bayer</td>
<td>Bauxite</td>
<td>350°F with 350 g/l NaOH</td>
<td>Al₂O₃</td>
<td>Very large</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Beaverlodge</td>
<td>Complex uranium ore cont.; pyrite, pitchblend, chalcopyrite, etc.</td>
<td>220°F @ 80–90 p.s.i.g. air Na₂CO₃ solution</td>
<td>Na₂UO₄</td>
<td>500 tons/day ore treated</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>Metallurgical Resources, Inc.</td>
<td>Cobaltite–Co 12%, Fe 19%, Ni 3%, As 45%, S 20%</td>
<td>? °F @ 120 p.s.i.g. air in 50% NaOH soln.</td>
<td>Na₂U₃O₈</td>
<td></td>
<td>17</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>19</td>
</tr>
</tbody>
</table>
HYPER-ATMOSPHERIC EXCLUSIVE METALLURGY

Because many of the early problems with this process were mechanical in nature, I would like to touch on some of the design developments which I believe are most significant in the successful application of pressure leaching.

The high pressure pumps required to feed the autoclave leach systems were a very serious problem in the early stages of development. For reasons which are still obscure, the wear rate on all types of piston pumps in this service was excessive even when fitted with tungsten carbide inserts. This problem has been solved for high feed rates by the Freeport Sulfur Company in connection with their Moa Bay Project. Their development work, in cooperation with two manufacturers of high pressure diaphragm pumps and later with a major oil company, resulted in three reliable types of hydraulic displacement diaphragm pumps capable of either 250 gal./min or 500 gal./min of slurry at 600 p.s.i.

For low feed rates, successful operation was achieved with an air displacement-type pump developed in 1958 by the Calera Mining Company. This unit, essentially a multichamber automatic blow-case, eliminated the possibility of hydraulic oil contamination of the autoclave in the event of diaphragm failure. In a leach system involving oxygen, this would be a decided advantage.

Mechanical abrasion, impeller corrosion and leakage through rotary seals are always problems in pressurized autoclave systems.

The vertical tower-type reactors developed by Freeport Sulfur Company eliminated this problem. Their pressurized "Pachuca" type reactors, using a titanium draft tube and 650 p.s.i. steam, very effectively provided the necessary agitation. This same general technique should be applicable to sulphide concentrates using air in place of steam. Limited developments along these lines were undertaken by Chemico. With this design, it should be possible to achieve limited countercurrent flow of the oxidizing gas and concentrate slurry. This would be particularly advantageous if oxygen were substituted for air.

Controlling the flow of leached slurry from the autoclave was a difficult problem. The energy release in this single stage reduction from autoclave conditions to atmospheric ranges from about 200 to 1400 ft. lb. of energy per pound of slurry, depending on the temperature and pressures employed. When these slurries are expanded under flow-control restrictions, a substantial portion of this thermal energy is converted into mechanical energy resulting in extremely high slurry velocities. Very few materials are known that will withstand this service. At Freeport Sulfur, standard four-pass floating head heat exchangers with titanium tubes, tube sheets and channels were successfully used to reduce the slurry temperatures. On the cooled slurry, high density alumina gave good service. Using this approach, substantial energy is recovered as low pressure process steam. Successful operation has been reported by Mancantelli with tungsten carbide flow control valves on the carbonate uranium leach autoclaves at Beaverlodge. At Calera, high density alumina, nitride-bonded silicon carbide and titanium were found satisfactory as mentioned in Table 2.

For acid services, carbon brick set with C-6 cement was found remarkably resistant to attack either by corrosion or abrasion both at Moa Bay and Calera. At Calera, the leach autoclave partitions were replaced with this
material early in 1956 and no detectable wear was observed after three years of service even though the full stream of the agitators impinged directly on the compartment walls.

As a result of the progress over the past ten years on this process, we can proceed with some degree of certainty on future applications of pressure to extractive hydrometallurgy. Likewise, through the efforts of those engaged in the study of the reaction mechanisms and kinetics of these processes, we have a far better understanding of the chemistry involved.

The current status could be summarized as follows: the design specialists in this field know how to build a successful plant, the scientists associated with this field of chemical metallurgy have a reasonably good understanding of the mechanism of the reactions and the probable rôle of various process parameters for any given ore or concentrate, but the economists have yet to prove conclusively that the process can compete on the world market.

FUTURE HYPER-ATMOSPHERIC EXTRACTIVE METALLURGY

And now, concerning the future of extractive metallurgy at hyper-atmospheric pressures, I believe that expansion will occur ultimately in the following fields:

(i) high value oxide ores;
(ii) metallurgical residues from conventional extractive methods;
(iii) the recovery of complex alloy scrap.

It is doubtful that this process can successfully compete with existing smelting and refining operations on sulphide ores. Where the mineral deposits are geographically far removed from existing smelting and refining facilities and the sulphide ores are amenable to pressure leaching and hydrogen reduction, the situation may be quite different.

For any process, two basic conditions must be satisfied. These are:

(i) the total process system must be technically sound and proven in principle;
(ii) the over-all economics are such that the process can compete on a free market without subsidy or other economic concessions.

Both of these criteria are influenced by the demands of an expanding economy and the impact of new research in all related fields of science and engineering.

Over the past 25 years, we have seen a gradual depletion of the higher grade ore deposits, while at the same time, a rapid increase in consumption of practically all metals. This trend will undoubtedly continue. Thus, we will become more dependent on extractive metallurgical methods which can treat low grade ores that are not currently amenable to the more conventional methods. The Freeport Sulfur developments on the laterite iron ores of Moa Bay clearly demonstrate the utility of pressure leaching on such ores and may well serve as a guide for future expansion of this type of operation. Likewise, its large scale application to uranium as, for example, the Eldorado Mining and Refining Ltd, at Beaverlodge, further substantiates this point.
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Both of the above operations, as well as the Bayer Process, have a number of factors in common that appear to dictate the use of pressure techniques in preference to all others. These are:

(i) large tonnage ore reserves;
(ii) ores cannot be concentrated by any currently known flotation process;
(iii) production rate requirements are high, thereby justifying large continuous or semi-continuous process equipment;
(iv) other processes are either not available, or are less attractive, for a variety of reasons, than pressure leaching.

For mineral deposits, then, where the above conditions are similar, we may expect, ultimately, additional expansion of pressure leaching using large capacity, well-integrated plants on the less common metals of high economic value, such as uranium, nickel and possibly cobalt. Nickel and cobalt in serpentine and laterite ores will probably be the principal areas of expansion in the future, using acid circuits for low magnesia and ammoniacal systems for high acid consumption ores at low or moderate pressures. In time, low-grade oxidized copper ores may be attractive candidates for the application of pressure leaching.

The second field in which I anticipate substantial progress is in the application of pressure for the dissolution of metallurgical residues from other processes. Recent work by Pearce, Warner and Mackiw28 has clearly demonstrated the technical feasibility of pressure leaching and hydrogen reduction for dissolution and reduction-separation of nickel-copper-cobalt-iron matter of varying compositions. This same approach is particularly attractive for speisses, providing an acid circuit is employed. With sufficient iron to convert the arsenic as ferric arsenate, the usual disposal problems are nonexistent.

The pressure leaching is very effective for the dissolution of mixed hydrosulphides of nickel and cobalt obtained from the cementation process of cobalt-nickel separation invented by De Merre28,30. After removal of the excess of sulphur present in this residue by roasting or distillation, the sulphides are completely converted to cobalt and nickel sulphates in under slightly acid conditions at 350–400°F with 50 p.s.i.a. O₂ overpressure.

Concerning the recovery of metals from scrap, an ammoniacal process has been developed and used by Whitaker Metal Company for recovery of pure copper from copper base alloy scrap. Some years ago, promising preliminary results were achieved at Howe Sound with acid pressure leaching of finely divided residues and small scrap of alloys, such as S–816 and N–155. Here, the tungsten and columbium remained in the residue while the cobalt, nickel, chromium and part of the iron went into solution. Solvent extraction proved promising for their subsequent separations. Alloys of this class represent an extremely difficult metallurgical problem because of the number of elements in the alloy. Their high level of contamination usually precludes direct scrap recycle.

The use of pressure leaching and, perhaps, hydrogen reduction, to treat metallurgical residues will, I believe, become increasingly important. Here, where tonnages are small, batch processes may prove quite suitable. The
pressure processes may well complement the existing techniques and treat a number of problem residues.

I expect two quite opposite developments in the future; first, the large, integrated plant operation on low grade oxide ores of high intrinsic value not economically amenable to any conventional process, and second, a relatively small plant, even, perhaps, on a batch basis, to handle high grade metallurgical residues from current extractive processes.

Pressure leaching and hydrogen reduction in direct competition to existing pyro- and electrometallurgical processes is hard to evaluate. Its praise or condemnation has often been based more on emotion than on sound scientific and economic judgement. Each has its advantages. In the following table, I have attempted to summarize some of the factors that will influence the selection of pressure leaching—hydrogen reduction versus conventional processes for future installations.

A direct economic comparison of the two extractive methods is not possible from published cost data.

Improvements that have been, and will be made, in supporting technologies will substantially influence the future of hyper-atmospheric hydrometallurgy. The continuing downward cost trend of tonnage oxygen suggests its reconsideration. By the replacement of high pressure air with oxygen, a substantial reduction of total operating pressure is possible. This would result in lower installation and operating costs for compressors and reduced mechanical problems. It is unfortunate that at the time the Calera plant was equipped for oxygen leaching, no sustained period of operation was achieved because of other problems, including some with the oxygen plant itself.

![Figure 4. Percentage of cobalt extracted in 30 minutes v. temperature-oxygen concentration](image)

Since the over-all rate of extraction is a complex function of temperature and oxygen concentration, it is usually possible to obtain equivalent results at lower temperatures but higher oxygen overpressures with a net reduction in autoclave operating pressure. This relationship is shown in Figure 4 for Calera Concentrates.
<table>
<thead>
<tr>
<th>Metallurgical factors</th>
<th>Chemico process</th>
<th>Smelting and refining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals applicable</td>
<td>Ni, Co, Cu</td>
<td>Cu, Pb, Zn, Ni, Co, Au, Ag, Se, Te, Cd</td>
</tr>
<tr>
<td>Recovery of precious and less common metals Au, Ag, Pt, Sc, Ti, Cd</td>
<td>No concentration effect; cyanide treatment of leach residues possible on alkaline circuits; reagent cost will limit applicability</td>
<td>Trace quantities concentrated and recovered from cell slimes, dust collector residues, etc.</td>
</tr>
<tr>
<td>Concentrate grade and variation of grade</td>
<td>Some variation possible, but feed to leach circuit must be maintained reasonably constant to optimize autoclave chemistry and recovery</td>
<td>Substantially greater tolerance for concentrate grade variation; depends on smelting operations employed</td>
</tr>
<tr>
<td>Ability to separate metals Co/Ni</td>
<td>Excellent for wide range of Co/Ni ratios; selective H₂ reduction; less attractive for 50/1 Co/Ni or 50/1 Ni/Co systems</td>
<td>No separation possible in smelting; De Merre Process will yield Ni-free Co; hypochlorite ppt. if Co to yield 1/110 Co/Ni anodes</td>
</tr>
<tr>
<td>Purity of product</td>
<td>Equivalent to smelting and refining except in some grades; sulphur will be high on calcium containing ores in acid circuits</td>
<td>Higher purity possible in some process if required; i.e. OFHC Cu</td>
</tr>
<tr>
<td>Physical state of product</td>
<td>Powder—directly convertible to rolled formed shapes in case of Cu; Co and Ni available in compacted briquettes</td>
<td>Cast billets, slabs, wire, bars, shot, sheared cathodes, etc.; continuous cast shapes; powder not normally available</td>
</tr>
<tr>
<td>Marketable by-products</td>
<td>(NH₄)₂SO₄</td>
<td>H₂SO₄, elemental S, Au, Ag, Pt, Se, Te, Au?, Cd, etc., depending on ore and process</td>
</tr>
<tr>
<td>Residue and gas disposal problems</td>
<td>None, including arsenical ores</td>
<td>Molten slag; SO₂ air pollution; problem of disposal of As for arsenical ores</td>
</tr>
<tr>
<td>Fuel, power and raw material requirements</td>
<td>Fuel</td>
<td>Fuel</td>
</tr>
<tr>
<td></td>
<td>(1) Process steam</td>
<td>(1) Roaster</td>
</tr>
<tr>
<td></td>
<td>(2) Propane for H₂ production</td>
<td>(2) Reverberatory furnaces (very large; nat. gas or fuel, oil)</td>
</tr>
<tr>
<td></td>
<td>(3) Natural gas and steam (ammonia synthesis)</td>
<td>(3) Holding furnaces and anode casting</td>
</tr>
<tr>
<td></td>
<td>Power</td>
<td>(4) Process steam</td>
</tr>
<tr>
<td></td>
<td>(1) Leach circuit compressors (air)</td>
<td>(5) Fire refining</td>
</tr>
<tr>
<td></td>
<td>(2) Hydrogen compressors</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) Process equipment</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raw materials</td>
<td>Power</td>
</tr>
<tr>
<td></td>
<td>(1) (Ammonia)</td>
<td>(1) Tank house—(large power requirement)</td>
</tr>
<tr>
<td></td>
<td>(2) S for H₂S</td>
<td>(2) Cathode melting furnace</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3) Process equipment</td>
</tr>
<tr>
<td>Plant characteristics: minimum plant size</td>
<td>~ 2000 t/year metal</td>
<td>Raw materials</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1) Plating agents</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Power and fuel requirements substantially larger)</td>
</tr>
<tr>
<td>Process surge capacity</td>
<td>Very limited unless large solution storage capacity available</td>
<td>Large—minimum size depends on process; a least factor of 10 larger than minimum pressure leach-reduction process</td>
</tr>
</tbody>
</table>
New materials of construction and their adaptation to this process system will also tend to improve the future economies of the system.

I feel that we have approached the point in time where the two basic process philosophies can merge and complement each other. Likewise, there are a number of potential regions where a combination may result in over-all improvements. A few of the many possible combinations that should be considered are:

(i) pressure leaching—electrowinning;
(ii) atmospheric leaching—high pressure hydrogen reduction;
(iii) pressure leaching—chemical precipitation—pyro-reduction.

References
24 Blair T. Burwell. “Salt Lake Tungsten Co. custom plant treats low grade concentrates to produce synthetic scheelite”, *Mining World* 17, 44 (1955).
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