# Extractive metallurgy techniques possibly applicable in India

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METALLURGY remained an art from the time of Agicola (credited with having written the first treatise on the subject) to the end of the 19th century. In many areas, it remains an art to this day. This does not mean to imply that no advances have been made in metallurgy. But there are many examples of early metallurgical work which our best scientists today find difficult to explain. An outstanding one is that of the Delhi Pillar at Kutub Minar forged of iron, as far as is known, about the 12th century and still standing, almost unweathered, in upright position a few miles outside the city of New Delhi. During the present rocket race, a great deal of scientific work has been done on the metallurgy of steel and special alloys, with the result that ductilities and tensile strengths have increased dramatically within the past twenty years.

Table I[1] shows India's production, exports and imports of various minerals and metals. From this it will be noted that, while India imported only 8 to 10 per cent of the iron needed annually, usually in the form of special shapes or alloys, it was necessary to import almost the entire amount required of the copper, lead, nickel, tin and zinc. In addition to this, considerable quantities of cryolite are required for the manufacture of aluminium, even though India is self-sufficient in bauxite, the raw material which is primarily required in the manufacture of aluminium. Because India's balance of payments is considerably on the debit side, she can ill afford the foreign exchange required to import these materials even though they are becoming increasingly important to the development of an integrated industry.

There are three approaches, which can be taken to alleviate the situation: exploration, substitution and development of new extractive technigues.

## Exploration

Exploration is a must and a new procedure for India is now being carried out by the Airborne Mineral Surveys described by Dr K. Jacob[1], which has recently completed a coverage of 90 395 sq. kilometers in Rajas-

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## SYNOPSIS

*The author in this paper has reviewed the accepted practice and some of the newer methods which are under development or have been put into practice recently for the recovery of copper, lead, zinc, uranium, molybdenum, nickel and cobalt in the light of conditions to be encountered in India such as difficult transportation of raw materials and finished products, inadequate power distribution and the psychology of Government and labour. Among the newer processes to be considered are: the nitric acid, sulfuric acid and ammonium carbonate cycles for hydrometallurgy, large scale pyrometallurgical processes, bacterial leaching and electrolytic processes for treatment of leach liquors. The underground leaching process as proposed by Kennecott is discussed briefly.*

than, Bihar and Andhra Pradesh. Ground exploration of some of the several thousand anomalies indicated by the survey is now being followed up. The work should be continued until all the areas of India likely to contain commercial minerals have been covered by detailed exploration to determine what deposits and at what grade the elements needed might be available. The particular value of modern techniques unavailable to the ancient prospector is that they disclose various information such as conductivity of the rocks underlying alluvial and other shallow covering material.

Because India is an old country and the ancestors of the present occupants were not without ability in the discovery and mining of metals, it is likely that the best and the most accessible deposits were discovered long ago and perhaps were mined out. On the other hand, there is evidence that India entered the iron age sometime before Europe did so. It may be that the metals necessary for the manufacture of bronze, including copper, lead, zinc and tin might not have been completely exhausted and that new deposits will be found in the general vicinity of the old mines. This is a question which can only be answered by the results of a comprehensive exploration for these metals.

TABLE I Production, export and import of selected minerals and metals by India (metric tons)

| Minerals and metals | Production | | | Export | | Import | |
|---|---|---|---|---|---|---|---|
| | 1963 | 1965 | 1966 | 1965–66 | 1966–67 | 1965–66 | 1966–67 |
| *Aluminium* | | | | | | | |
| Ore | 565,000,000 | 707,000,000 | 750,000,000 | 70,000,000 | 92,000,000 | — | — |
| Metal | — | — | — | — | — | 62,883 | 143,604 |
| Barytes | 37,312 | 48,283 | 51,663 | 5,000 | 5,000 | — | — |
| Coal | 66,000,000 | 67,000,000 | 68,000,000 | — | — | — | — |
| Copper | — | — | — | — | — | 333,225 | 379,107 |
| Chromite | 65,000 | 60,000 | 78,000 | 27,000 | 70,000 | — | — |
| Feldspar | 20,933 | 26,771 | 26,400 | — | — | — | — |
| *Iron* | | | | | | | |
| Ore | 20,504,000 | 23,738,000 | 26,508,000 | 11,985,000 | 13,206,000 | — | — |
| Metal | — | — | — | — | — | 969,493 | 897,419 |
| Pyrophyllite | — | 11,828 | 8,294 | — | — | — | — |
| Ilmenite | 26,000 | 30,000 | 30,000 | 28,000 | 30,000 | — | — |
| Manganese Ore | 1,296,000 | 1,647,000 | 1,678,000 | 1,331,000 | 1,185,000 | — | — |
| Nickel | — | — | — | — | — | 18,617 | 13,163 |
| Platinum | — | — | — | — | — | — | — |
| S. Steel | — | — | — | — | — | — | — |
| Tin | — | — | — | — | — | 71,687 | 63,252 |
| Zinc | — | — | — | — | — | 128,374 | 104,243 |
| Mica | 25,000 | 24,000 | 22,000 | 43,000 | 19,000 | — | — |
| Dolomite | 1,070,000 | 976,000 | 1,047,000 | 40,000 | 26,000 | — | — |
| Steatite | 121,000 | 156,000 | 148,000 | 10,000 | 10,000 | — | — |
| Kyanite | 31,665 | 37,481 | 63,670 | 33,000 | 36,000 | — | — |
| Sillimanite | 11,285 | 11,276 | 10,286 | 6,000 | 5,000 | — | — |
| Sulphur | — | — | — | — | — | (1963) 261,018 | (1964) 241,161 |
| Rock phosphate | 13,127 | — | — | — | — | 297,683 | 449,407 |
| Gypsum | 1,188,000 | — | — | — | — | 46,339 | 84,533 |
| Cryolite | — | — | — | — | — | 2,746 | 1,916 |
| Asbestos | 2,712 | — | — | — | — | 36,958 | 35,710 |
| Lead | — | — | — | — | — | 57,268 | 99,630 |

## Substitution

Every effort should be made to substitute more abundant metals in India for the ones that are scarce. It is encouraging to note from the NML annual report[2] and previous papers that considerable work is being done on hot-dip aluminising of iron and steel, development of nickel-free austenitic stainless steel and preparation of synthetic cryolite so as to minimize the import of some of the critical materials. It is doubtful, however, that sufficient substitution can be practised to eliminate the necessity for the importation of considerable quantities of copper, lead, zinc, nickel and tin. If sufficient and large enough deposits of these metals are discovered by exploration, India's problem will be solved, at least temporarily. If only low grade deposits or even high grade but limited deposits are discovered it will be necessary to pursue vigorously the third possibility.

## Extractive techniques

The best assurance to minimize the deficit cost of purchase of the base metals is to develop methods for extracting these from low grade ores—possibly lower grade ores than ever used commercially before. This is not India's problem alone but that of most of the world. Normally, one expects to work an ore deposit at a profit. In fact, one of the definitions of "ore" is "a combination of minerals that can be mined and treated at a profit in spite of a lot of mismanagement". In India's case, the balance of payments may make it worthwhile to work materials of lower grade, even on a subsidy basis. It may be recalled that some 50 or 60 years ago copper deposits containing 8 to 10 per cent copper were available in various parts of the world. It was considered uneconomical to work anything having a grade below 2 or 3 per cent. A few years ago mining was started on the huge Bingham Canyon copper deposit in Utah, U. S. A., the ore running about 1 per cent copper, using open cut methods and found to be worked profitably. Since this breakthrough, many other large deposits of porphyry copper have been worked at profit with a percentage of copper as low as 0.5 per cent. Contrast between the two extremes can be seen readily in Australia where Mt. Isa maintains a cut-off grade of about 3 per cent copper by deep mining methods, while Mt. Leyell in Tasmania works an ore running 0.4 per cent copper and still shows a profit. The difference arises in the mining method used, the quantity of ore handled and the metallurgical treatment.

Before discussing specific methods for the treatment of low grade ores, it will be worthwhile pointing out some of the conditions in India which must influence the choice of such methods.

In India which is a tremendous country with few railways and insufficient revenue to maintain proper highways, transportation is one of the biggest problems. Consequently, one of the first considerations in any projected approach to the mining and processing of low grade ores should be that raw materials required to be transported should be almost nil and that the product should be of high enough grade that it can be economically transported to the point of use. Let us look for a moment at the conventional process for the production of copper. Normally, copper is mined as an oxide or sulphide ore, the oxide usually appearing nearer to the surface, with increasing sulfide content in the lower reaches of the mine. The ore is ground in water at about 70 to 80 per cent solids to something in the neighbourhood of 200 mesh for liberation of the economic minerals and then floated, usually using a xanthate as a flotation reagent. If a combination of oxide and sulfide material is present the 'leach-precipitate float', method is used to recover the oxide copper. In this process, the ore after floating out the sulfide is leached with sulfuric acid and the copper precipated by the addition of iron to the slurry. The copper containing slurry is then re-floated to recover the small grains of metallic copper. The concentrates are combined and if molybdenum is present, the flotation reagents are removed by steaming or the concentrate is treated with cyanide to depress the copper and the molybdenite is floated out.

The copper concentrate is smelted by a number of methods, the most common being the reverberatory furnace to produce a copper sulfide melt or matte and then blown with air in convertors using a silica flux to remove as much iron as possible. The blister copper is poured into anodes which are electrolysed to produce a high purity electrolytic copper for use in wire bars or sheet. Considerable equipment and raw materials are required to be hauled to the site of the operation of such a process. First, tremendous plant in the form of crushers, grinding mills, flotation machines, and other processing equipment, must be set up at the mill site. These must be supplied with crushing plates, balls and mill liners of steel, which are consumed at the rate of one to five pounds of iron per ton of ore ground, depending upon the abrasive nature of the material and fineness of grind. Before and during flotation, the pH must be adjusted by the addition of lime and this must be available in considerable quantities. Silica flux must be supplied to the convertor in the ratio of 2 or 3 times the weight of the copper produced. Power must be available for electrolysing the copper or the blister copper must be shipped out to the point where power is available for refining. Consequently the transportation of equipment and materials becomes a formidable one in a country like India. If the deposit is large enough and profitable enough such expenditure can be amortized and justified. If the deposit is marginal, there will be considerable question as to whether or not these expenditures can be recovered.

Lead and zinc processing requires somewhat similar flow sheets as they generally are recovered by sulphide flotation. The zinc is roasted to the oxide, usually in hearth, flash or fluid bed roasters while the lead is reduced in the blast furnace by the use of coal or coke. Generally, these operations are performed separately on the individual concentrates. The recent development in England of the Imperial smelting Process, in which the products from a mixed concentrate
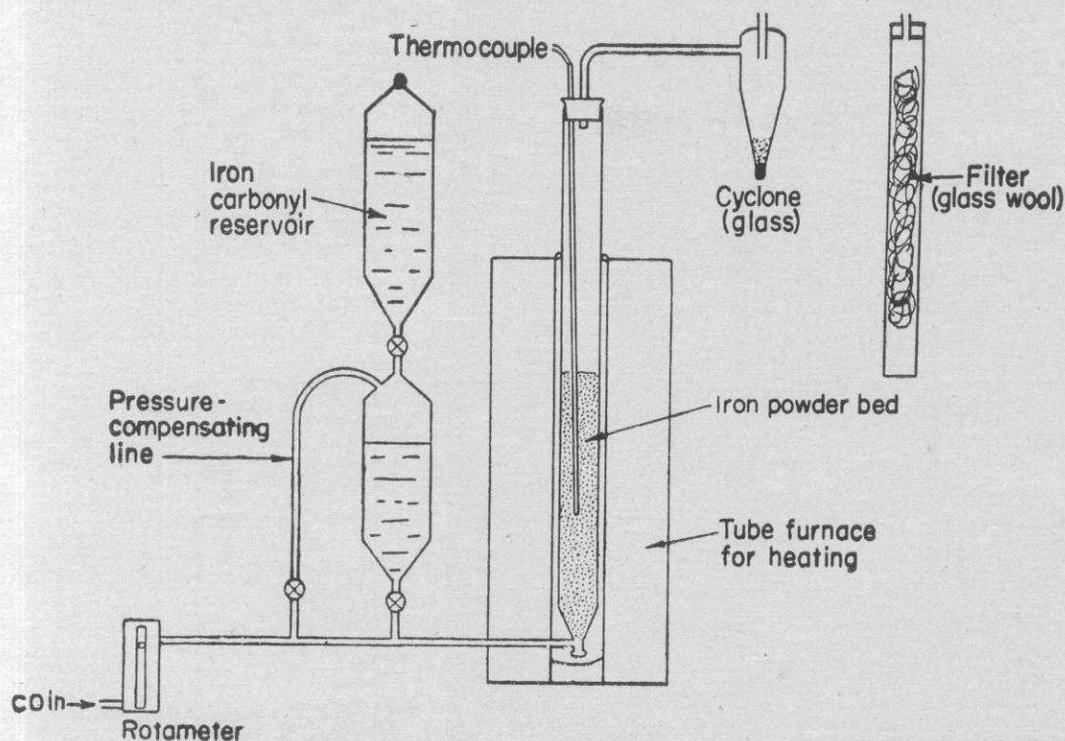
1 *Sketch of atmospheric pressure fluidized bed system for decomposition of iron carbonyl and condensation of iron product*

in a single blast furnace can be recovered in a bath of lead, has been making inroads into lead and zinc processing. Where appreciable silver, cadmium, indium and sometimes small amounts of gold must be recovered, the I.S.P. is not used because of better control of impurities during electrolysis. In mining and processing lead and zinc large amounts of equipment and material must be brought to the site and the product usually shipped out either as a concentrate or metal containing valuable impurities for further refining elsewhere. While pure lead is relatively easily recovered from a smelting procss, zinc is generally electro-refined to produce a high purity material. Consequently, a source of power is necessary. A retorting process in which the roasted zinc concentrate is mixed with coke, reduced and refined by volatilization can be used for high purity concentrate. The first zinc retorting plant in the world known to have been operated was at Zawar near Udaipur. Today, one of the best electrolytic zinc plants known is operating in the same vicinity.

The recovery of tin from cassiterite is usually a simple smelting process, but it does require coke and fluxes such as sodium carbonate. Molybdenum and tungsten, being high priced materials, can usually pay the cost of shipping a high grade concentrate so that they are seldom refined at the mine. Molybdenum usually occurs as sulphide, molybdenite ; the oxide molybdenite, sometimes occurs along with the sulphide. Tungsten occurs in two forms :

1. Calcium tungstate or scheelite, and
2. the series of iron tungstate-manganese tungstate, known as wolframite, having two end members ferberite or iron tungstate and hubnerite or manganese tungstate.

The method used in processing of the tungsten minerals will depend on their composition. Generally molybdenite is roasted to the oxide $MoO_3$ leaving as little sulphur residual as practical. The product or roasted concentrate containing about 90% $MoO_3$ can be smelted by the thermite process to give a ferromolybdenum containing about 60% Mo or can be reduced in an electric furnace by carbon to give a ferromolybdenum containing about 80% Mo. It is logical to assume that in India where aluminium is more readily available than electric power, the thermite process will be preferable.

Tungsten likewise must be converted to the oxide before further processing. But the procedure is much more complicated than that for molybdenum. Generally, it is necessary to digest the tungsten ore with sodium carbonate at high temperature during which digestion the tungsten is converted to sodium tungstate. Through a series of steps, the sodium tungstate is then converted to ammonium tungstate which is ignited to leave the oxide $WO_3$.

For use in the manufacture of tungsten carbide the oxide is reduced with carbon under controlled condi-

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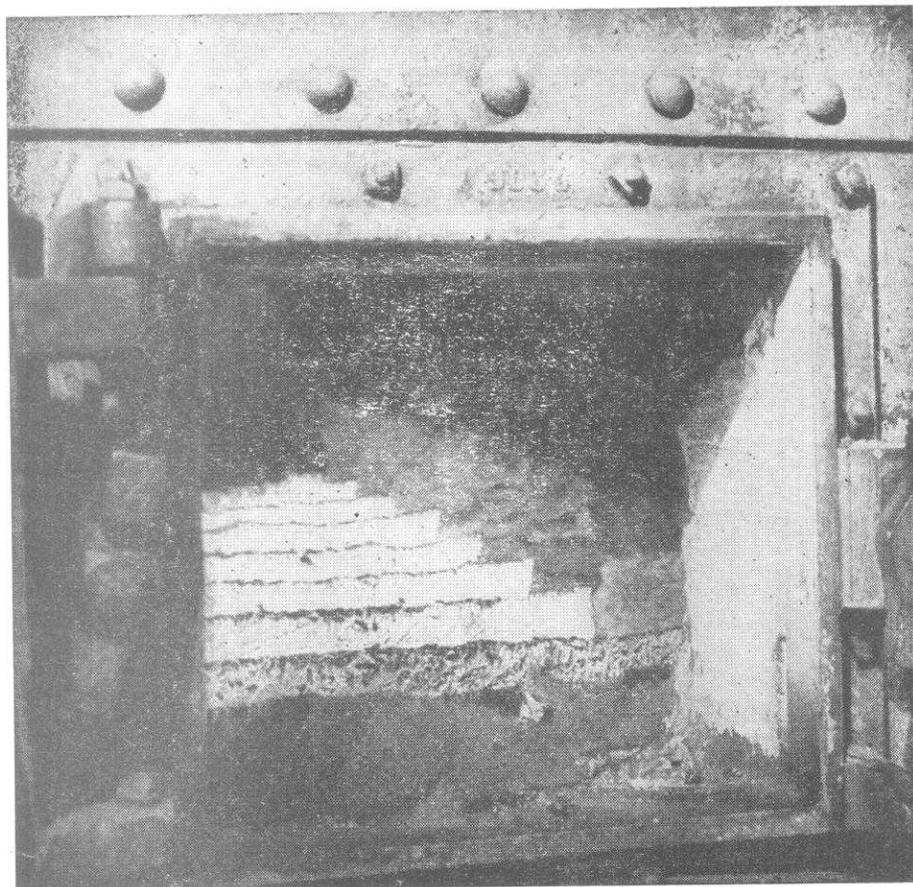
2 *View through the door of an Aerreshoff roaster*

tions, compacted and sintered with cobalt to produce the hard material used in cutting tools, in commerce. If ferro-tungsten is desired it may be produced directly from scheelite by either the thermite or electric furnace route. The hubnerite end of the iron tungstate-manganese tungstate series can be treated with hydrocloric acid to remove the manganese and leave a relatively pure $WO_3$ which can be processed to produce ferro-tungsten.

This brief review of the conventional methods for treatment of the metals in which India is now deficient is included for the purpose of indicating the complexity of converting the raw mineral to the desired product, for use in manufacturing. These processes, which have not changed appreciably for the last 50 years, present a challenge to India, to develop simpler, more efficient and less material consuming processes to make practical the extraction of these metals from lower grade ores which may be discovered or which almost certainly will be required to be used in the future industry of India. For this reason, it is proposed to review today some of the most recent processes which have been developed, some on commercial scale, some in pilot plant and some as yet only laboratory curiosities. These are discussed, not because they are necessarily the

processes of the future, but to stimulate the thinking in India which is going to be largely responsible for the development of practical processes for the utilization of the Indian raw materials. The processes, that will be discussed, are briefly :

1. Simultaneous autogenous roasting and leaching of sulphide ores, and direct production of metals from leach solutions by hydrogen reduction or electrolysis.
2. Ammonia or ammonium carbonate leaching of oxidized copper, nickel and uranium ores.
3. Sulphuric acid leaching of copper, zinc, uranium and nickel ores.
4. Nitric acid leaching of copper, lead, zinc, uranium, nickel and cobalt ores.
5. Fluidized bed operations in extractive metallurgy.
6. Ion exchange and solvent extractions.
7. Underground leaching.

### Fluidized bed operations

The most widely applied on plant scale of the recent developments in extractive metallurgy is the fluidized bed. The first work was done around the 1940's by
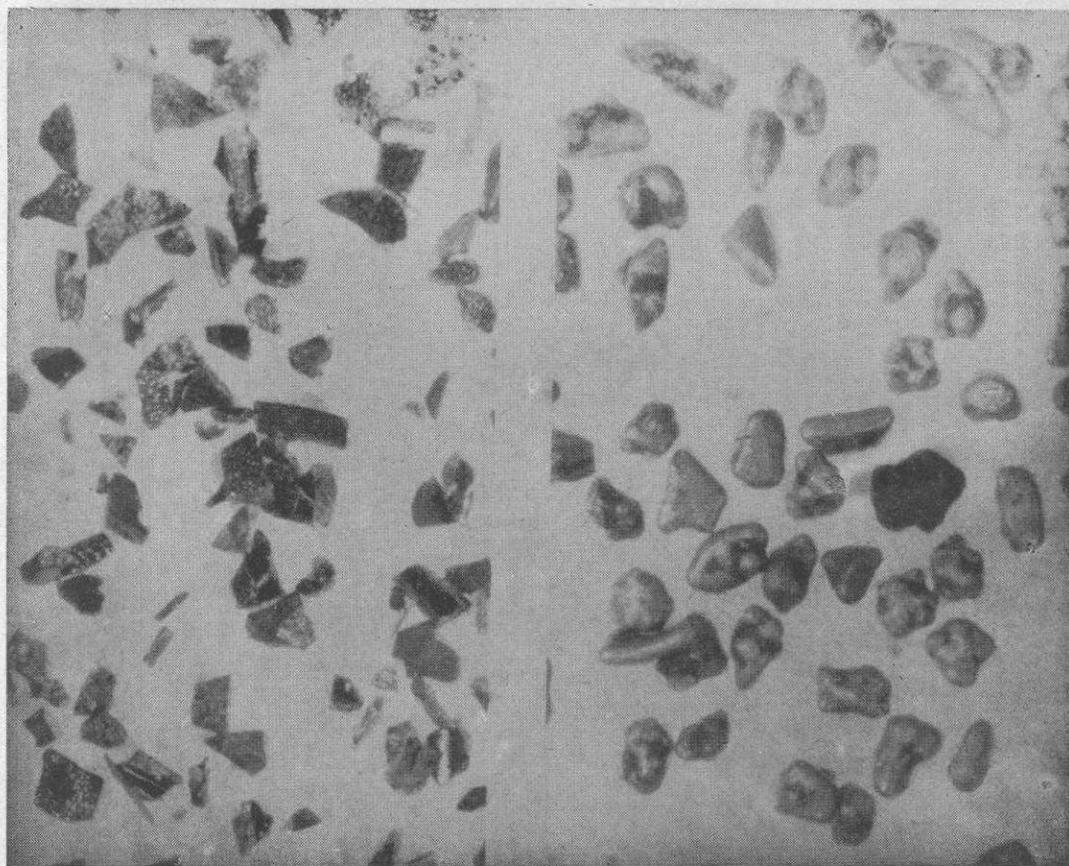
**3A** *Iron particles making up the original fluidized bed*

**3B** *Similar particles after a few minutes iron deposition*

the oil companies who used a bed of catalyst for cracking heavy oil fractions, passing the vaporized oil up through the catalyst bed along with hydrogen and collecting the lighter oils and gases from the product. The Dorr Oliver Company took over the patent rights to apply the process to metallurgy and for a number of years have been the leaders in building commercial reactors. Most of these are in operation to roast sulphides, such as pyrite. Pyrite reacts with air, beginning at about 700°F and proceeds more vigorously with a rise in temperature. Fig 1 shows a diagram of a small laboratory fluidized bed reactor for the deposition of iron formed during the decomposition of iron carbonyl $Fe\,CO_5$. Fig. 2 is a view taken through the door of an Herreshoff roaster. It shows variations in temperature, as indicated by the differences in colour, between the ridges and furrows of the material being roasted. Temperatures may vary as much as 300 or 400°F within the roaster, and give rise to incomplete combustion in some cases and excessively high temperatures in others. The particular view shown is a molybdenum roaster where temperature is quite critical to obtain a residual sulphur meeting a specification of 0·1%. If the temperature rises above about 1300°F, the molybdic oxide product becomes sticky and makes operation of the

roaster difficult. Fluidized bed roasters have the advantage that they may be held within a few degrees of the set temperature. A more uniform contact between solids and gases permits homogeneous completion of the reaction. Various types of reactions including dead roasting of sulphides, sulphate roasting[3], reduction roasting and decomposition of compounds are readily carried out in the fluid bed. Sulphate roasting,[3] for example, has become important when pyrite or other iron sulphides contain small amounts of cobalt, nickel or copper. By careful adjustment of the temperature it is possible to obtain a 95% decomposition of the ferric sulphate to form ferric oxide and leave almost all the cobalt, nickel and copper behind as soluble sulphates. These can then be leached with water. One difficulty in the case of roasting chalco-pyrite, a copper-iron sulphide, is the formation of copper ferrite which is not amenable to leaching. This formation of the complex is more apparent at higher temperatures. A rather unique use of the fluidized bed is in the decomposition of chemical compounds to leave the metal as a residue to build up on the original bed particles.[4] Fig. 3 shows iron particles making up the original fluidized bed which were prepared by fracturing flakes of iron deposited from iron carbonyl on the inside of

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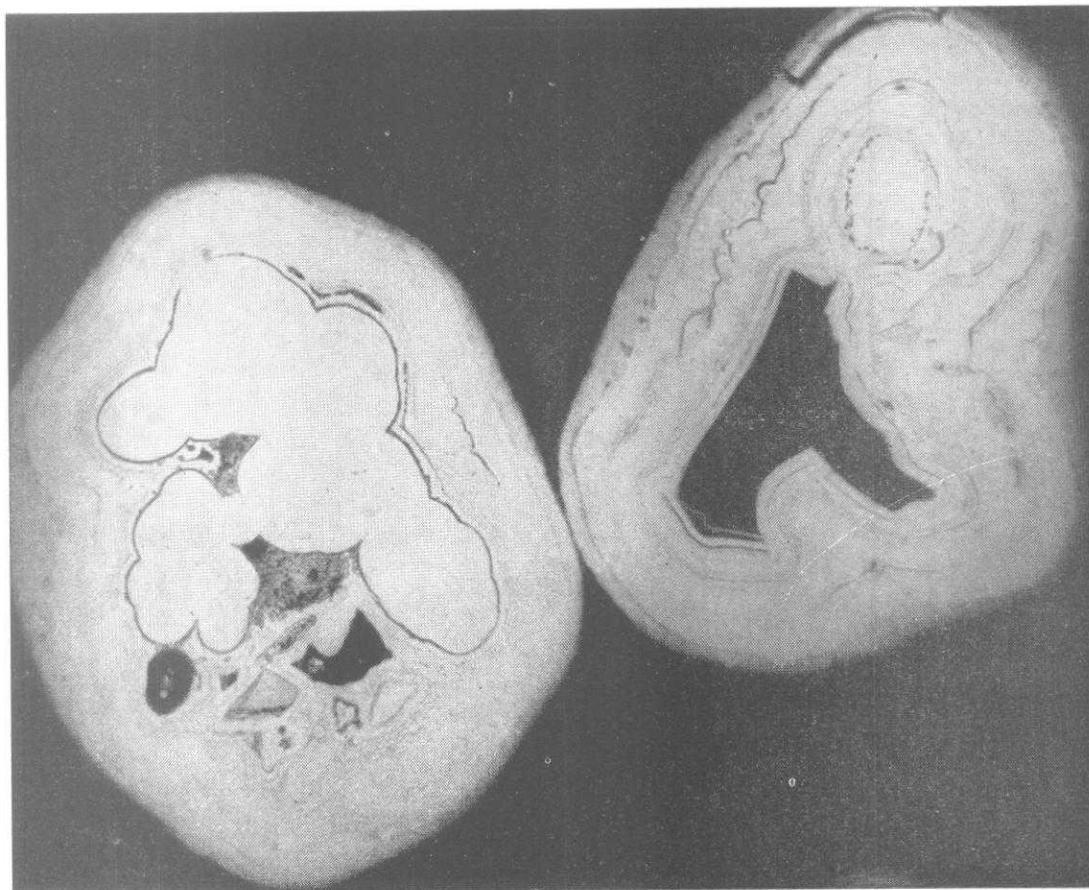
4  *Enlarged cross-section of some of the particles showing layers of carbonyl iron built up during decomposition*

a tube. The accompanying picture of the finished bed product shows clear evidence of the deposition of iron on the particles, rounding of the corners with some increase in particle size. Fig. 4 is an enlarged cross section of some of the particles showing the layers of carbonyl iron as these build up during the decomposition.

Laboratory attempts at reduction of titanium tetrabromide by hydrogen failed because of small amounts of nitrogen contained in the hydrogen being used as a reductant. When the hydrogen was passed through a heated titanium getter, the bed welded so that it was almost impossible to separate the particles of titanium. It appears that so long as sufficient nitrogen was present, the surface of the titanium produced was a nitride but as soon as nitrogen was eliminated pure titanium must have been deposited and this welded at the prevailing temperature (about 1400°C). At the time this experiment was run, in 1959, we were not too familiar with the deposition of material from a fluidized bed and were not aware of the possibility of increasing space velocity to a point at which normally sticky particles may not cause de-fluidization of the bed. So far as we are aware, no one has continued the work on the reduction of titanium bromide with hydrogen, though the economics would appear to be much better than the use of sodium or magnesium as the reductant.

The decomposition of iron carbonyl[5] in a fluidized bed is extremely interesting, because it opens up the possibility of using a carbonyl process for the production of high purity iron from laterites containing nickel and other impurities. Iron ore can be reduced by hydrogen, treated with carbon monoxide to form mixed carbonyls of iron and nickel, which are separated by distillation. Each can then be decomposed independently to form a high purity nickel and a high purity iron without the objectionable residual materials that usually build up in scrap. The fluidized bed has the advantage over the ordinary roaster of other processing equipment in that it contains no moving parts inside the heated zone. Heat can be supplied directly by the combustion of gas where this is not deleterious to the product, or the bed material can be circulated to a heated bed and the heat introduced with the hot material. In this way, the oil companies are able to heat a catalyst by combustion of the tarry residue in an oxidizing bed, then feed the catalyst into the gas stream to supply heat necessary for the hydrogenation cracking of the oil under reducing conditions. Fluidized beds have been so well accepted that to spend more time on the subject would probably be repetitious.
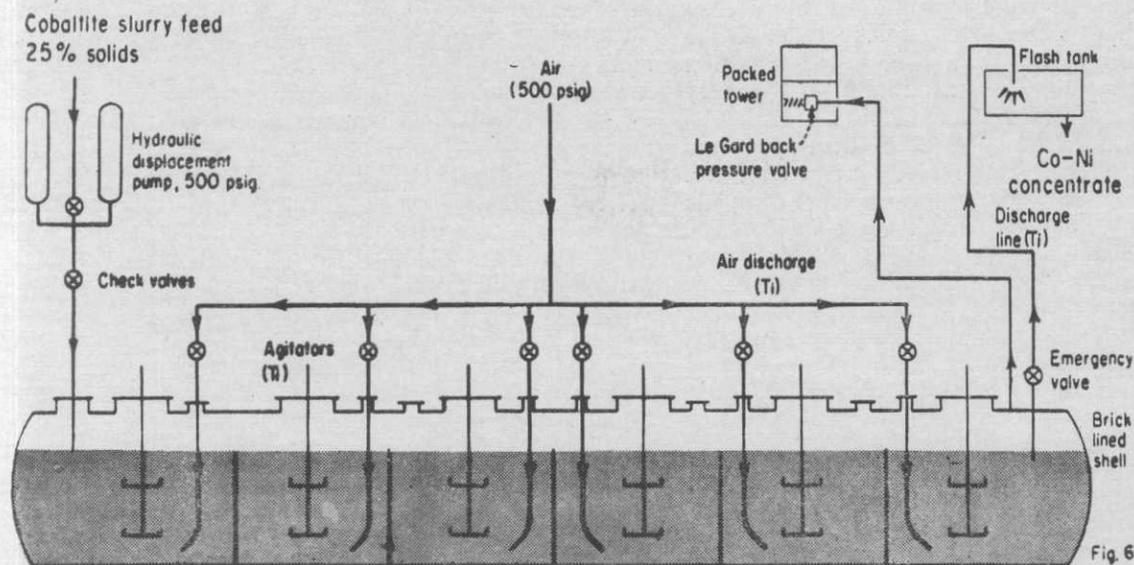
5 *Sketch of the autoclave used in the Garfield Plant*

## Ammonia or ammonium carbonate leaching

The ammonia or ammonium carbonate leach was first introduced by Carron[6] in the Nicaro Nickel Refining Plant built by the United States in Cuba during World War II. The ore treated was a laterite containing approximately 1 to 1·5% nickel and balance mostly iron and chromite. It operated satisfactorily during the war but did not show a profit on the investment. Afterwards, the plant was sold and then operated by Freeport Sulphur until Mr. Castro expropriated it. Reports from the engineers on the project indicated that it was economical so long as it was unnecessary to amortize the capital cost of the plant, already paid by the United States Government. The ore was roasted with a reducing agent such as carbon or coke to completely reduce the nickel and much of the iron. It was then digested with ammonium carbonate to put the nickel into solution. Some of the cobalt was also recovered but the chromite was essentially unattacked. The nickel contained in the serpentine fraction underlying the laterite deposit apparently did not respond to the treatment.

During the uranium boom in western United States the Battelle Memorial Institute[7] investigated the possibility of ammonium carbonate leaching of uranium, which has a particular advantage in the case of ores which contain high percentages of lime. These ores consume a large amount of sulphuric acid in the conventional acid leach. At Battelle, leaching towers, operating under an exhaust pressure of about 100 pounds per sq. inch, were fed by a high pressure pump at the bottom of the first tower. The pulp density was 40 to 60 per cent solids and the pulp flowed by gravity from one tower to the next. Agitation was maintained in the system by bubbling air, ammonia and carbon

dioxide through each tower. The discharge slurry or pulp contained the uranium in solution as uranium carbonate, which is quite soluble under the condition employed. The solids were separated by thickening and filtration to give a clear filtrate containing the uranium. The filtrate was then heated with steam to flash out the ammonia and $CO_2$ and precipitate the uranium as $UO_3$. This process was run as a small pilot operation at Battelle and has been described by McDonald[6] and others. An interesting aspect is that only make-up reagents are required, most of the ammonia and $CO_2$ being recovered for recycle.

## Pressure leaching

Pressure leaching of sulphide ores first gained interest when the Chemico Company designed and put into operation a plant at Garfield, Utah, USA[8] for the recovery of cobalt from concentrates obtained from the Sunshine Mine in Idaho. The novelty of the process lies in the fact that the sulphide is actually burnt in a slurry or pulp of water and sulphuric acid under conditions of high temperature and high pressure. Fig. 5 is a sketch of the autoclave used in the Garfield Plant, 40 feet long and 8 feet in inside diameter. The outside shell was 10% stainless steel clad, about an inch and a quarter in thickness. This was lined with sodium-silicate-impregnated asbestos sheet and then a layer of acid-proof brick was laid with acid-proof cement inside this. Slurry was pumped into the autoclave by Mantin Gaulin pumps normally used for homogenization of milk and never intended for the type of service to which they were exposed in this operation. The result was considerable wear, stoppage of valves and erosion. Pressure inside the autoclave was approximately 500 lbs per square inch and the temperature

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was 425°F. Initial temperature was attained by use of super-heated steam whereupon the combustion of the cobaltite concentrate began, from then on the operation was autogenous. The slurry was found to be very corrosive, the sulphuric acid concentration reaching as high as 200 gm/litre. Stainless steel developed the appearance of Swiss cheese after a few months' service. The only thing that saved the autoclave from complete destruction was the acid-proof brick layer inside. The cobaltite concentrate contained, in addition to the sulphide, a large quantity of arsenic which was one of the reasons for the choice of this particular process. The arsenic, during the leaching and subsequent treatment with lime, was converted either to ferric or calcium arsenate, both of which are insoluble and can be safely stored in a tailings pond. Air was used for oxidation of the concentrate and the residual nitrogen blown out through a let down valve into a spray tower. The procedure was quite complex but eventually a solution containing the cobalt, a small amount of iron, some copper and saturated with calcium sulphate was obtained. The iron was removed by oxidation with air after making the solution ammoniacal. Copper was recovered by cementation on cobalt powder and some of the calcium sulphate was filtered out after preheating the solution before it entered the reduction autoclaves. The inverse solubility of calcium sulphate at high temperatures made this partially successful. However, it was never possible to obtain a finished cobalt product with low enough residual sulphur to meet specifications. Reduction was accomplished at about 600°F by introducing hydrogen into the solution in another autoclave. Nucleation was required to get the formation of the cobalt product as individual particles rather than as a coating on the walls of the autoclave. Eventually, the hydrogen reduction step was abandoned in favour of electrolytic production of cobalt metal. About the time that the plant was operating satisfactorily, the Belgium cobalt interests decided to cut the price to $ 2 per pound, which made the Garfield Plant uneconomical to operate. This is being referred to here primarily because of technical interest and because it has served as a model for several other plants including Sherritt Gordon[9] operating on an ammoniacal cycle and the Freeport Sulphur plant for recovery of nickel, under construction in Moa Bay, Cuba, about the time Castro took over.

*Ion exchange*[10]

Some of the first work on ion exchange was done at Ames, Iowa, during separation of the rare earths. Its operation depends upon the ability of certain materials like the zeolites and synthetic resins to selectively absorb certain ions from solution, leaving the remainder behind. The absorbed ion is then eluted from the resin in much the same way that an ordinary water softener removes calcium, iron and magnesium from water and gives these up to a concentrated salt solution for regeneration. Ion exchange has been extensively used in the purification and concentration of uranium solutions and one or two small operations have been run on the recovery of copper. Because of the present high cost

of selective resins, the process is not economical for lower-priced material. If the resins were developed and made in India the production costs might be lowered so that they could be used to recover more metals at prices comparable with those now being imported.

*Solvent extraction*[11]

Solvent extraction has largely replaced ion exchange in many operations where its use is practical. An organic liquid containing the solvent is brought into intimate contact with the solution containing the desired metal ion, and a transfer to the organic phase occurs. After settling, to separate the two liquid phases, the organic liquid is stripped by treatment with another aqueous solution. In this way it is possible to increase the concentration of the metal to a considerable extent and the original solvent solution can be used again. This method has been successful for the separation of titanium tetrachloride from some impurities and zirconium from hafnium to which it is closely related. A solvent extraction process developed at the Australian Mineral Development Laboratories permitted the separation of scandium in relatively large quantities from a rare earth titanate by-product from treatment of Radium Hill Uranium Ore in South Australia.

*Underground leaching*

A new technique is being considered by the Kennicott Copper Company in the United States. They have an oxidized copper deposit too deep to be mined profitably by the underground method. They propose to drill down to the bottom of the deposit and detonate an atomic bomb. According to previous tests of this type of explosion, depending on the size of the bomb, this should yield, during the time of explosion, a sphere possibly 200 feet in diameter when the bomb pressure reaches the lithostatic pressure of the surrounding rock. At this point, the force of the explosion is completely contained. The internal pressure decreases as the products of the explosion condense to a glass, covering the bottom of the chamber. At this point, there is no longer a pressure to support the roof and this caves in, forming a chimney, filled with broken rock until the void space between the broken rock equals that of the original sphere formed during the explosion. The broken rock will contain the oxidized copper ore and it is proposed to drill another hole into the chamber and pump the leach solution through this to dissolve the copper. The copper would be recovered by normal chemical methods or by electrolysis and the leach solution re-circulated through the broken rock in the chamber. This experiment is scheduled for some time in 1969 and may possibly lead to an entirely new concept of treatment of deeply buried bodies of ore for which a suitable leaching solution can be devised.

*Cyclic processes*

It is the writer's opinion that the so-called "cyclic pro-

cess" holds most promise for the economical recovery of metals from low grade ores. A cyclic process is one in which a material containing a valuable constituent is treated to remove this constituent by a reagent which is regenerated simply during formation of the final metallic product or compound. We have previously touched on the ammonium carbonate cycle and carbonyl process.

In addition, under the right conditions, sulphur dioxide leaching, sulphuric acid treatment of ores and the nitric acid cycle can be considered the more important of the cyclic processes. These are applicable to various metals, depending on the reagent. The amount of make-up required depends upon the reagent and the materials present which tie up this material as inert compounds, non-recoverable for recycle. For example, sulphuric acid and sulphur dioxide are often tied up by high lime ores to form calcium sulphate or calcium sulphite, which is seldom worth recovering. These two processes, however, have proved useful in the recovery of manganese[12] and uranium[13], aluminium and molybdenum. Two cyclic processes, which probably have received less attention than they deserve, are the carbonyl process and the nitric acid cycle.

The carbonyl process was developed by Mond when he found that carbon monoxide attacked nickel piping and valves. It is still used by the International Nickel Company in their Clydach Plant in England for the separation of cobalt and nickel. No other process gives as satisfactory separation of these two elements, the reason for this being that nickel carbonyl, $Ni (CO)_4$ is a very volatile compound while cobalt carbonyl is solid at room temperature. Work done at the Battelle Memorial Institute[5] a few years ago indicated that a cyclic process, based on the carbonyl principle, could be used for the extraction of nickel from lateritic iron ore and could produce a satisfactory nickel and an iron containing less than $0.05\%$ nickel. Further consideration of this process indicated the possibility of high purity iron for addition to a blast furnace or open hearth which would be free from the usual contaminants found in scrap iron. In this way, special alloys can be manufactured free from the deleterious residuals which plague the makers of these alloys.

The laterite is reduced in a current of hydrogen to produce a mixture of metallic iron and metallic nickel which are in turn treated with carbon monoxide under slight pressure to form the respective carbonyl. These are then separated by distillation and decomposed to produce the pure materials, at the same time releasing the carbon monoxide to be used for further production of carbonyl. The chief raw material required for the process would be the hydrogen used in reduction of the ore.

The nitric acid cycle has still more appeal for use in India. It was developed and run on a pilot scale in Patterson, New Jersey, by Dr E. S. Nossen[14] in an effort to convince the U. S. Government that low grade manganese ores could be upgraded to produce battery grade manganese dioxide at a reasonable cost. Unfortunately, some of the equipment in the pilot plant was inadequate for the operation and the project was abandoned before sufficient information was ob-

tained. Later, the Battelle Memorial Institute revaluated the process and found that the cost of make-up nitric acid was extremely low, approximately $ 1.00 per ton of ore treated. A manganese ore, which must be in a reduced state, is treated with nitric acid in stainless steel vessels at a pH of about 0.1. When the reaction is complete, the nitric acid is neutralized with calcium hydroxide and the slurry is filtered to leave behind iron, aluminium and silica from the ore and to produce a filtrate containing calcium and manganese nitrates. The solution is evaporated to form a syrup and then fed into a fluid bed using super-heated steam as the fluidizing gas and controlling the temperature at the decomposition point of manganese nitrate to produce manganese dioxide and calcium nitrate which can be leached out of the residue to give battery grade manganese dioxide. The calcium nitrate is decomposed at a higher temperature to recover the nitrate as nitric acid or nitrogen oxide which can be passed through a conventional tower with air to reproduce the nitric acid required for recycle. Most of the metals in which we are interested form soluble nitrates ; therefore leaching efficiency is excellent. About seventy-five per cent of the nitric acid is recovered directly from the steam condensate from the decomposition fluidized bed. The balance can be re-converted to nitric acid with an efficiency of approximately $98\%$ so that the overall loss of nitric acid is very small. For this process, almost no raw materials need be shipped to the plant site. For a small operation, tank car ammonia can be oxidized to give make-up nitric acid, or for a larger operation a Haber process plant for the production of ammonia can be installed. This paper has not attempted to be in any way comprehensive but to put forth some of the newer processes which are being developed or are under consideration. It is hoped that the scientists in India will be enough interested to follow through on some of these, take advantage of the possibilities that seem to lie in their use. The author while visiting the Trombay installation noted that considerable work was under way on materials needed in reactor construction such as zirconium[15], tantalum and columbium. Work is also on hand on the use of the alumino-thermic reduction for the production of tantalum and other metals.[16] This is another process that has great potential and has yet never been fully investigated. A few years ago the author took out a patent[17] on the use of liquid oxygen in thermite and has since made several tests to evaluate the potential of the process. It was found that with the proper conditions it is possible to melt tungsten by alumino-thermic reaction and production of silicides and borides presents only minor difficulties.

It is a human failing for one visiting a country for a short length of time (such as the present author who has been in India since July 2, 1968) to wish to say what he thinks should be done, without adequate background for really knowing whether or not his conclusions are valid. He may therefore be pardoned for one or two observations : It seems extremely necessary that the scientific manpower of India be used as efficiently as possible and this, it appears, is not being done. Too

many science graduates find it difficult to find jobs either for the Government or in the private sector and consequently are drawn away to Canada, the United States or to England. Without being an expert on economics it is difficult to advise as to how these people are to be re-attracted to India ; but the fact remains that without their help and advice, progress in the production of the very necessary base metals and other requirements in which India is short, will be greatly impeded. The scientists in India compare favourably with those anywhere in the world. With the required backing from Government and industry, these scientists could within 10 to 20 years bring India up to par with most of the industrialized countries. In Australia, for instance, the problem is somewhat different from that in India. Australia has a limited population and vast distances to transport goods. Consequently, it is difficult to produce the small quantities of goods required at a reasonable price. The contrary is true in India and every effort should be made to produce goods in volume at as low a price as practical and to pay the workers as much as can be spared to still make a reasonable profit for the owner. In this way, the worker will be able to purchase the goods and the Government will be able to tax the profits so that the money available for scientific research and development will continue to flow, not necessarily from foreign sources, but from within India itself.

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