Economic utilization, recovery and substitution of some strategic non-ferrous metals

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WITH the increased tempo of industrial expansion and the ever rising consumption of common non-ferrous metalslike copper, lead, zinc, tin, deficient in India, their conservation, substitution, reclamation from waste products and substandard raw materials are of paramount importance for India, not only to tide over the present crisis but also in the larger interest of economic growth and self-sufficiency. Self-sufficiency can be attained by developing processes for the utilization of low grade and other complex ores, recovery of metals from waste products like slags, ashes, drosses and above all by the conservation of non-ferrous metals not available in the country by their judicious use and substitution.

Though India is endowed with extensive ore deposits of iron, manganese, ilmenite, thorium, zirconium, bauxite, etc., that are not only sufficient for the future needs but can build up substantial export trade, there are acute deficiencies in some of the major non-ferrous minerals such as zinc, copper, lead and nickel. The general position of the heavy surpluses and acute deficiencies are depicted below :

Surplus reserves which can be utilized for export

Aluminium, Magnesium, Rare metals, Cerium group, Strontium, Iron, Manganese, Titanium, Thorium and Zirconium.

Fair reserves

Beryllium, Hafnium, Lithium, Chromium, Tantalum, Vanadium and Uranium.

Insufficient for our requirements

Zinc, Copper and Lead.

Acute deficiencies

Antimony, Cadmium, Germanium, Molybdenum, Platinum, Tin, Bismuth, Cobalt, Mercury, Nickel, Selenium and Tungsten.

The National Metallurgical Laboratory has been engaged on studies pertaining to the economic utilization and recovery of metallic values from low grade ores, reclamation of waste materials and substitution of strategic non-ferrous metals.

Utilization of low grade ores

In view of the increased demand of the common non-ferrous metals and the heavy drain of the foreign exchange, there naturally follows urgent need to undertake studies on the low grade chromite, vanadium, nickel and cobalt ores found in abundance, and some of the research investigations already in progress at the National Metallurgical Laboratory have yielded valuable results in this regard.

(i) Thermal beneficiation of low grade chrome ores

Though India possesses extensive deposits of chrome ores, the metallurgical grade ores are limited to only within a million tons. Besides the deposits in Orissa, which have Cr : Fe ratio of 2·8 : 1 to 4 : 1, almost all the other chrome ore deposits in India are of low grade. Such deposits are fairly widespread in the country, a major part occurring in the belt of Andhra Pradesh, Mysore and Maharashtra. Low grade deposits are also reported in Kashmir, Upper Assam, Manipur and Andaman islands.

The large reserves of low grade Indian chrome ores, having chromium to iron ratio less than 3 : 1, are unsuitable for the standard grade ferro-chrome. The Cr/Fe ratio of these ores are generally not upgraded

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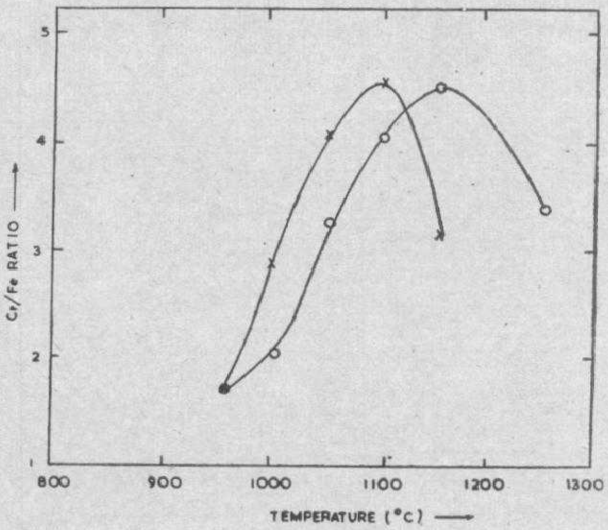
by normal ore-dressing methods to meet the specifications for metallurgical uses, since both chromium and iron are chemically bound in chrome spinel. A chemical attack on the spinel is necessary to remove as much of iron as possible from the ore, or to extract the chromium from the ore in the form of a suitable chemical compound for further processing.

Extraction of chromium from the ore can be carried out by chemically attacking the minerals either with alkalies, acids or by chlorination. Alkali processes convert the chromium in the mineral to chromates or dichromates which can be reduced to chromium sesquioxide for blending the low grade ores. Calcium chromate or calcium chromite has been reported to be sutiable for blending purposes.[1] The acid processes consist of leaching the low grade ore with sulphuric acid. Pressure leaching with insufficient acid produces a basic chromium sulphate which can be roasted to chromium sesquioxide or suitably electrolysed to yield metallic chromium. Chlorination has been attempted by several workers[2,3,4] for removal of iron from chrome ores. Yatlov ond Popva[5] have concluded that iron could not be separated without reacting chromium.

Thermal beneficiation of low grade chrome ores consist in either alteration of the ore or preferential reduction of iron from the ore followed by its subsequent separation. Alteration is carried out by melting the ore with a suitable flux which necessitates very high working temperatures; subsequent separation of iron can then be made by physical methods or by acid leaching. Selective reduction of the ore by electric smelting has been reported[6] to produce a chromium-rich slag with high Cr : Fe ratio and a high chromium pig iron as a by-product. Thermo-dynamic considerations[7] indicate that reduction of chromium at high temperatures becomes inevitable under normal conditions when carbon is used as a reducing agent. Selective solid state reduction can be carried out at a comparatively lower temperature without reducing chromium oxide. The metallic iron can be removed leaving behind a chromium-rich residue with high Cr/Fe ratio.

Systematic research work was undertaken at the National Metallurgical Laboratory utilizing gaseous[8] as well as solid carbonaceous reducing agents for selective solid state reduction. The reduced iron was subsequently removed by leaching with dilute sulphuric acid. A high Cr/Fe ratio with good chromium recovery could thus be attained.

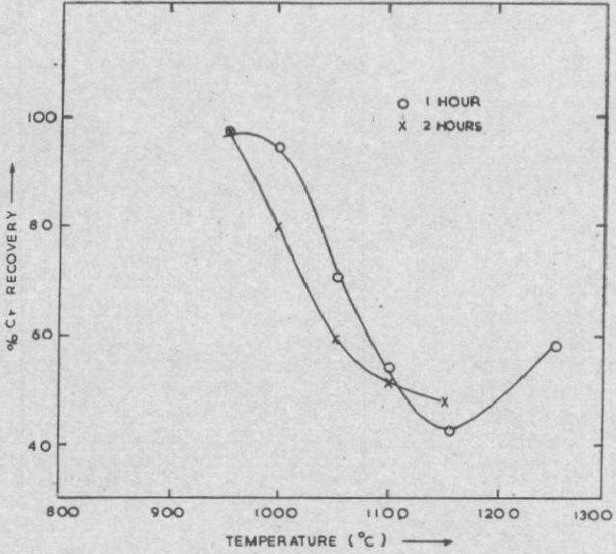
A low grade chromite from Mysore containing 48·38% Cr_2O_3, 22·91% FeO, 3·07% Fe_2O_3, 11·09% MgO, 5·45% Al_2O_3, 6·08% SiO_2 with a Cr/Fe ratio of 1·66 : 1 was crushed to —5 mesh B.S.S. sieve for gaseous reduction. Reduction was carried out with a coke oven gas analysing 51% H_2, 23% CH_4, 2·2% other hydrocarbons, 9·7% CO, 3·8% CO_2, 9·6% N_2 and 0·7% O_2 at temperatures varying from 950°–1250°C. It was observed that with the increase of time and temperature of reaction, Cr : Fe ratio initially rises to 4·6 and thereafter falls due to the greater reduction of chromium oxide. The effect of temperature of reduction on the Cr/Fe ratio and percentage of chromium recovery, after 1 and 2 hours of reduction are represented in Figs. 1 and 2.



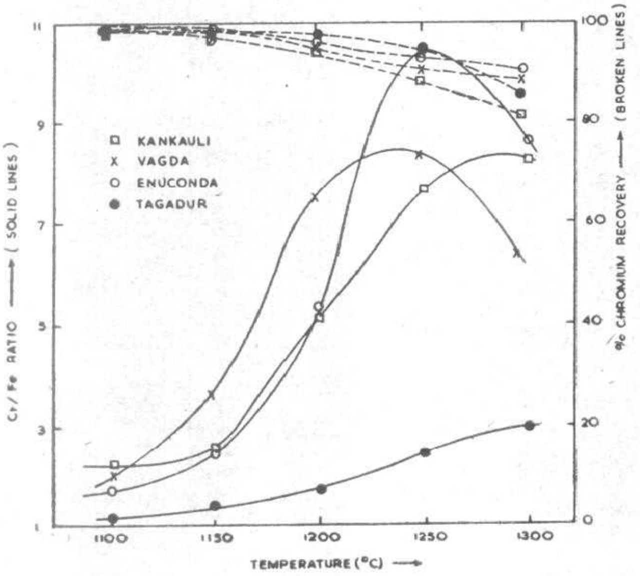
1 *Effect of temperature on Cr/Fe ratio during gaseous reduction*

The studies on gaseous reduction of Mysore chromite with Cr/Fe = 1·66 indicate that it is possible to upgrade the ore to the standard specification after roasting in presence of coke oven gas for one hour at 1100°C and leaching the reduced product with 10% hot sulphuric acid. This process gives a product with Cr/Fe ratio of 4 : 1 and a chromium recovery of 80%.

The studies wtih solid reducing agents revealed that they were more selective and systematic studies were carried out using coke. Four different ores from Vagda and Kankauli areas of Ratnagiri district, Maharashtra, Enuconda deposit of West Godavari district, Andhra



2 *Effect of temperature on chromium recovery during gaseous reduction*



3 *Effect of temperature of reduction on beneficiation of chrome ores*

Pradesh and from Tagadur area of Mysore were investigated for thermal beneficiation.[9,10,11] The ore from Tagadur area was reduced without preliminary concentration while table concentrates of the other three samples were used for reduction. The chemical analysis and initial Cr : Fe ratios of the four samples are recorded in Table I.

TABLE I Chemical analysis of some low grade chrome ores studied

	Chemical analysis					
Ores	%FeO	%Cr_2O_3	%Al_2O_3	SiO_2	%MgO	Cr/Fe ratio
Tagadur	32·66	38·6	4·4	10·6	11·8	1·01
Vagda	19·78	44·93	14·9	2·3	8·9	1·53
Kankauli	21·5	34·72	14·74	9·6	17·2	1·6
Enuconda	28·53	40·83	16·9	3·22	7·5	1·23

The effect of temperature of reduction on the Cr/Fe ratio and the chromium recovery is shown in Fig. 3. It was found that preliminary physical beneficiation of the ores greatly helps the subsequent thermal treatment. In fact, the preliminary dressing not only increases the energy economy of the process by eliminating unwanted gangue from the furnace burden, but also facilitates reduction and leaching due to removal of unwanted gangue materials.

It can further be observed from Figs. 1, 2 and 3 that in all the ore samples the Cr/Fe ratio initially increases with an increase in temperature of reduction to 1250°C and thereafter falls with increase of temperature due to simultaneous chromium reduction and its elimination during leaching operation. The predressed ores could be upgraded to a Cr/Fe ratio of about 8 or even higher by restricting reduction temperature to around 1250°C.

Attempt was made to suppress chromium dissolution in the leaching stage by controlling the acid content of the leach acid and almost complete chromium recoveries could be attained; this procedure greatly simplified the recovery of ferrous sulphate without appreciable chromium contamination.

The overall economics of the process can be further improved by the decomposition of ferrous sulphate to produce pigment grade Fe_2O_3 and sulphuric acid, from the SO_2 produced during roasting. Further, the product with Cr/Fe ratios as high as 8 : 1 can be blended with low grade ores to adjust the Cr/Fe ratio to 3 : 1, which can be used suitably for ferro-chrome production.

A process has also recently been developed at the National Metallurgical Laboratory, whereby it is possible to remove most of the unwanted iron from the chrome ore without resort to the use of acids for the removal of reduced iron.

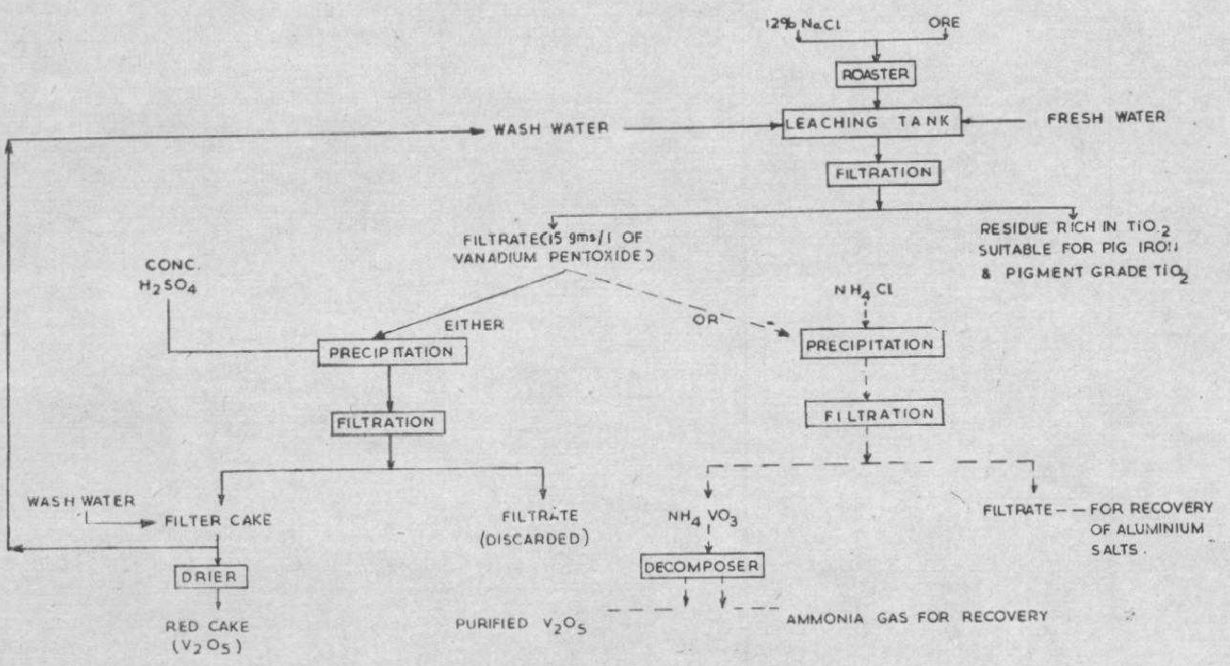
Production of vanadium pentoxide

The most important deposits of vanadium in India are the vanadium bearing titaniferrous magnetite deposits of South-Eastern Singhbhum and adjoining parts of Mayurbhanj district in Orissa. The vanadium content of these vanadium bearing deposits varies appreciably between 0·55 and 1·8% vanadium pentoxide[12], with an estimated reserve of 22 million tons. Vanadiferrous magnetites with an average of 0·56% vanadium pentoxide together with chromium oxide have also been found in Nilgiri Hills.

In view of the unfavourable mode of occurrence, the vanadium bearing ores are generally not amenable to simple ore-dressing methods and the only method is to attack the vanadium constituents chemically either by reduction to metallic state at elevated temperatures and subsequent removal of vanadium as oxide or by roasting with suitable fluxes to leach vanadium.

Systematic studies for the recovery of vanadium pentoxide from the ore containing 1·4% vanadium has been completed[13] and a pilot plant has been set up. The ore contained :

V	...	1·4%
TiO_2	...	13·12%
Fe	...	57·12%
SiO_2	...	1·2%
Al_2O_3	...	2·21%



4 *Flowsheet for the recovery of vanadium pentoxide*

The crushed ore was mixed with varying quantities of sodium salts like sodium carbonate, sodium chloride and sodium sulphate and roasted at 950°C. The different factors studied include (a) roasting with varying proportions of sodium carbonate and sodium chloride, (b) roasting with varying quantities of sodium salts, (c) temperature of roasting, (d) time of roasting, (e) particle size of vanadium bearing ore. It has been observed that sodium chloride is the best roasting medium for the maximum recovery of vanadium and 75–76% recovery is obtained by roasting the ore crushed to -72 mesh (B.S.S.) with 12% sodium chloride at 950°C for 2 hours. The roasted ore was leached with hot water and leaching at 70°–80°C for 3 hours with good agitation has been found to result in maximum recoveries. The leach liquor containing 15 grams per litre of vanadium pentoxide is vigorously agitated at a temperature of 80°$-$90°C at a pH of about 1·5 to 2 to precipitate 90$-$95% of vanadium from the solution.

Based on the laboratory scale experiments, a flowsheet of the process proposed to be followed on the pilot plant is indicated in Fig. 4.

The possibility of adopting electric smelting of vanadiferrous ores and subsequent oxidation of the pig to yield a vanadium rich slag has also been critically examined and in view of the large capital investment, the process was not found attractive.

A process has recently been worked, whereby it is possible to enrich the vanadium content, without resorting to electro-thermal reduction and it is felt that the process will be very economical to operate under Indian conditions. Further investigations are in progress and the basic process for the recovery of vanadium pentoxide by salt roasting will not be materially changed excepting that an enriched material will be handled for the recovery of V_2O_5.

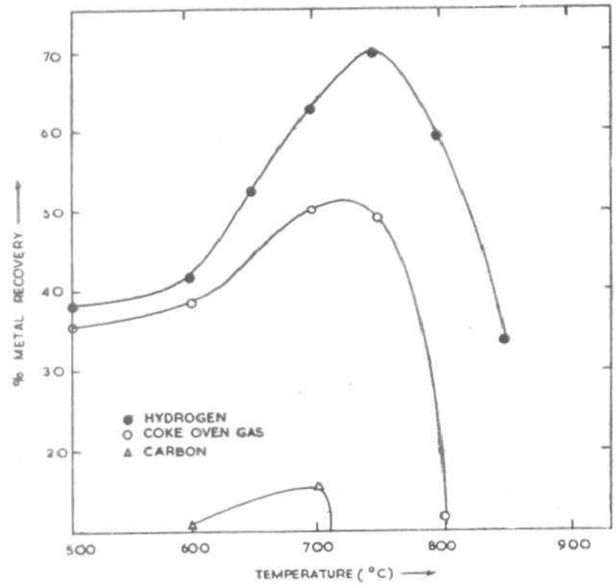
(iii) Recovery of nickel from low grade ores

Extensive survey work by G. S. I. has revealed several low grade deposits of nickel in India. Nickel occurs in the Serpentinous rocks of Assam and Rajasthan, lateritic ores of Keonjhar and Mayurbhanj in Orissa and copper ores of Singhbhum district in Bihar. In view of the strategic importance of nickel, systematic studies have been undertaken at the National Metallurgical Laboratory to recover nickel from the indigenous ores.

The low grade siliceous ores from Rajasthan and Assam have been examined in detail. Physical methods of beneficiation did not yield any encouraging results and chemical or pyro-metallurgical methods such as chlorination or roast reduction followed by ammoniacal leaching were investigated to recover nickel from these ores.

Chlorination with hydrochloric acid gas was attempted for recovering nickel from a sample of siliceous ore from Rajasthan containing 0·25% Ni, 5·24% Fe, 37·5% SiO_2, 39·6% MgO and 1·1% Al_2O_3. It was found possible to volatilise more than 95% nickel with 68% iron at 1000°C during an hour long chlorination. Results of chlorination at different temperatures are indicated in Table II.

A condensate containing nickel and iron in the ratio of approximately 1 : 14 was obtained within 45 minutes of chlorination at 1000°C with a nickel recovery of more than 95%. Chlorination provides possibility of



5 *Effect of temperature on nickel recovey*

extracting nickel and further studies under controlled conditions may prevent the contamination of iron in the condensate.

TABLE II Effect of temperature on chlorination of nickel ore

Temp. °C	% Fe chlorinated	% Ni chlorinated
800	32·5	22
850	44·2	32
950	66·3	87
1000	91·6	Complete

Roast reduction followed by ammoniacal leaching has also been investigated for the recovery of nickel from the siliceous ores. The lateritic ores of Cuba are already being exploited commercially by similar process, while the siliceous ores of New Caledonia were reportedly unsuitable for such treatment. The investigation at National Metallurgical Laboratory revealed that ammonia leaching process can be adopted for siliceous ores from Assam while a similar ore from Rajasthan with lower nickel content did not respond and only 44% of nickel was recovered.

The nickel bearing Serpentine from Assam containing 0·65% NiO, 38·34% SiO_2, 33·14% MgO and 10·86% Fe_3O_4 was successfully treated at the National Metallurgical Laboratory[14] using the ammonia leaching process and an overall 68—70% nickel recovery was obtained. Maximum extraction of nickel was achieved by reduction of the ore with hydrogen at 750°C, while coke or coke oven gas was less efficient and higher temperatures of reduction resulted in lower nickel dissolution due to formation of iron-nickel alloys. Experimental results obtained using different reducing agents and temperature conditions are recorded in Fig. 5.

The reduced nickel ore is crushed to −200 mesh (B.S.S.) size for efficient nickel extraction. Preconditioning of the reduced ore in a strongly ammoniacal slurry, prior to leaching helped in the corrosion and removal of the simultaneously reduced iron particles and greater nickel dissolution was achieved during leaching. The preconditioned ore is leached at room temperature under atmospheric pressure by continuous aeration and agitation in presence of a complexing anion. The complexing efficiencies of various anions were examined and the observed sequence of the effective anions is found to be,

$$CO_3^{--} > Cl^{-} > SO_4^{--} > OH^{-}$$

Leaching with a carbonate-rich liquor containing 7·5% each of ammonium carbonate and ammonium hydroxide has been found to be suitable and the leaching is complete within an hour. The complex nickel ammine solution obtained after filtration of the slurry was boiled to distil off ammonia and a basic nickel carbonate was recovered which could be calcined to nickel oxide. The ammonia leaching process can well be applied to other low grade nickeliferrous ores and based on the laboratory scale study a flow-sheet is formulated for pilot plant trials and shown in Fig. 6.

Extraction of nickel from lateritic deposits of Orissa is under study and the ammoniacal leaching process has been found to be well-applicable to some of these ores too.

Use of continuous fluo-solid reactors for reduction of nickel ores has yielded encouraging result in laboratory scale trials and a pilot scale fluo-solid reactor, which is under installation at the laboratory, will be used for trials as soon as it is complete.

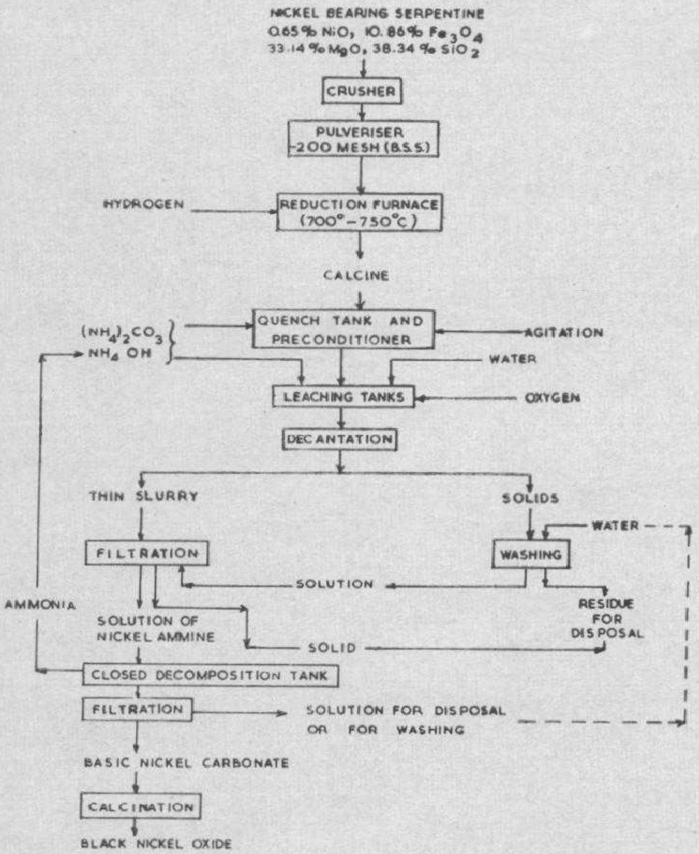
Nickel occurring along with copper and uranium in Singhbhum district is yet another important source of the metal. It is estimated that with the daily capacity of the Jadugoda plant at 1 000 tons there exists the possibility of extracting around 1 000 tons of nickel per annum which will save foreign exchange to the extent of 1 crore of rupees.

In short, there exists greater possibility now for indigenous nickel extraction than thought in previous years. Ways and means are being continuously worked out at National Metallurgical Laboratory both on laboratory scale and pilot plant.

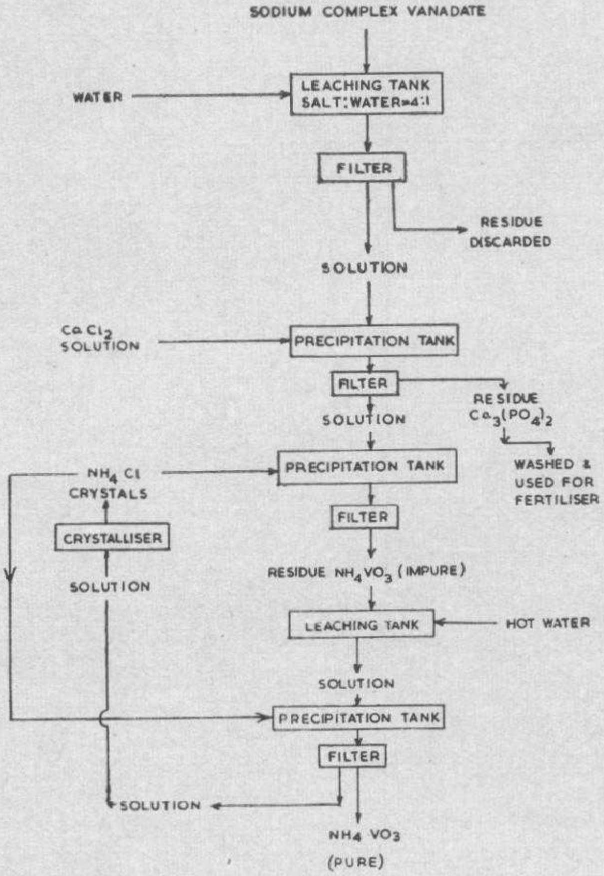
Conservation

In view of the scarcity of non-ferrous metals in the country, the development of new industries should be supplemented with conservation of scarce metals. This can be achieved by minimising waste, the recovery of metallic values from all waste materials and substitution. The losses of the metallic values during mineral processing may occur either during mining, mineral dressing, metal extraction and refining or finishing.

The National Metallurgical Laboratory has already



6 *Flowsheet for nickel extraction using indigenous low grade serpentine ores*



7 *Flowsheet for treatment of complex vanadate salts*

made outstanding contribution for the recovery of metallic values from waste products produced during the processing of ores or the metals, including the recovery of metallics from foundry ashes, drosses and skimmings and some of the investigations are briefly described.

(i) Waste products of the aluminium smelter

The Bayer's process for the recovery of alumina from bauxites results in the production of red mud—the leached residue of bauxite and the complex vanadium salts obtained from the soda recycle circuit. The alumina is also contaminated with traces of gallium oxide which affect the conductivity of the metal produced and if separated out the gallium oxide can serve as a useful material in addition to improving electrical properties of aluminium. These waste products from aluminium industries need to be properly utilized.

(a) Utilization of red mud : A sample of red mud containing 21·4% Al_2O_3, 4·8% SiO_2, 20·8% Fe_2O_3, 28·81% TiO_2, 7·8% CaO, 0·6%, MgO, 3·8% Na_2O, 12% L.O.I., and 0·08% V was tested for its suitability for Al_2O_3 extraction by lime soda sinter process.[15] Attempts were also made to separate iron from red mud by roast reduction followed by magnetic separation, the residue obtained after aluminium extraction was found suitable for the production of ferrotitanium.

It was observed that 80% Al_2O_3 could be recovered by roasting red mud with Na_2CO_3 and limestone in the proportion of 1 000 : 400 : 35 at 1100°C for 180 minutes, followed by aqueous leaching at 80°C for 1 hour, 1·5 to 1·7 gms SiO_2 also dissolved per 100 gms of alumina and this could be desilicated by recycling the aluminate solution in Bayer steps.

(b) Recovery of vanadium from complex vanadium salts produced at the alumina plant : The bauxite deposits of Lohardaga contained traces of vanadium that enters the Bayer's process liquor to an appreciable extent and its build up in the liquor affects the purity of the alumina. The regenerated liquor after precipitation of alumina is cooled to 25°C whereby vanadium separates as a complex salt containing phosphate and alkalies. The sodium complex vanadate thus produced has not been found to be of any use and the alkali content of this salt is recovered by lime addition by a process of

TABLE III Classification of non-ferrous scraps

Sl. No.	Scraps	Sources	Remarks
1.	Heavy scraps	Ingot discards, extrusion butts, plate and sheet scraps, off grade ingots and billets, defective castings, gates, runners, risers.	Recycled to plant circuit.
2.	Light scraps	Inspection and process scraps, e.g. shearings, clipperings, chips, stampings, etc.	Sorting and remelting can be used.
3.	Swarf	Turnings, borings, scalpings, saw dust, trimmings, soil scraps, etc.	Physical processes can be used.
4.	Drosses and skimmings	From melting shops, oxides or nitrides with entrapped metals (2–50%).	Physical and pyrometallurgical process can be used.
5.	Market scraps	Originally useful materials rendered useless through corrosion, wear and tear, breakage, etc.	Collection, sorting, cleaning and remelting can be used.

cationic exchange, resulting in a calcium complex vanadate salt. Investigations have been carried out at the National Metallurgical Laboratory to recover vanadium and phosphate from these salts and based on systematic investigations the flow-sheet of the proposed process is indicated in Fig. 7.

A similar product can also be obtained after acid leaching, phosphate separation and precipitation of ammonium vanadate by ammonium chloride for the calcium complex salts.

(ii) Recovery of waste products of the copper plants

Messrs Indian Copper Corporation are the only producer of copper in India and will soon be joined up by the two new plants in the public sector at Khetri and Rakha. Sulphur dioxide is a valuable by-product produced during roasting and converting. The adoption of Flash Smelting Process at Khetri is based on the recommendation of the National Metallurgical Laboratory and it is hoped that the sulphur dioxide formed will be used for the production of substantial quantities of superphosphate. Messrs Indian Copper Corporation is also adopting this process in their modernisation programme.

The chalcopyrites deposits of Singhbhum are associated with nickel and selenium and with the commissioning of the electrolytic refinery at Ghatsila, the nickel will be recovered from the electrolytic plant liquor. Investigations are also being carried out for the recovery of precious metals from the anode sludge.

The chalcopyrite at Rakha contain small percentage of molybdenum and it will be desirable to recover molybdenum from this deposit, even if the cost of operation is high.

The slag produced by the Flash Smelting process contains higher percentage of copper than that produced by the conventional process and it will be desirable to develop suitable methods—physical, hydro-metallurgical or pyro-metallurgical whereby the copper values may be recovered.

(iii) Secondary metals and their recovery

Excepting aluminium most of the non-ferrous industries in India depend on the import of primary metals and the recovery of secondary metals is of prime importance for the conservation of strategic non-ferrous metals. The wide range of non-ferrous scraps arising from the fabricators, founders, galvanizers, etc. may broadly be classified into five categories as indicated in Table III.

The clean heavy and light scraps can be recycled to plant process and circuit, usually after baling into convenient sizes in order to cut down the melting losses considerably. Clean and well sorted swarfs can also be conveniently briquetted for easy handling and melted. The recovery of secondary metals from clean scraps is being universally followed at most of the refineries.

Machine shop scraps are generally mixed up in small shops and recovery of metals from such mixed scraps and the surface oxides hinder the agglomeration of the melt. Melting with suitable fluxes, however, helps in metallic recovery. Large size of mixed scraps can be hand-sorted.

Various methods used to recover metallic values from the scrap include :

(i) melting down to an usable alloy ;
(ii) differential melting ;
(iii) thermal treatment with agitation ;
(iv) sigma oil method ;
(v) liquation or sweating ;
(vi) elimination of one or more elements by high melting alloy formation, immiscible in the molten phase ;

(vii) distillation of volatile elements ;
(viii) preferential leaching ; and
(ix) selective matte formation and elimination of other non-matting elements from the melt.

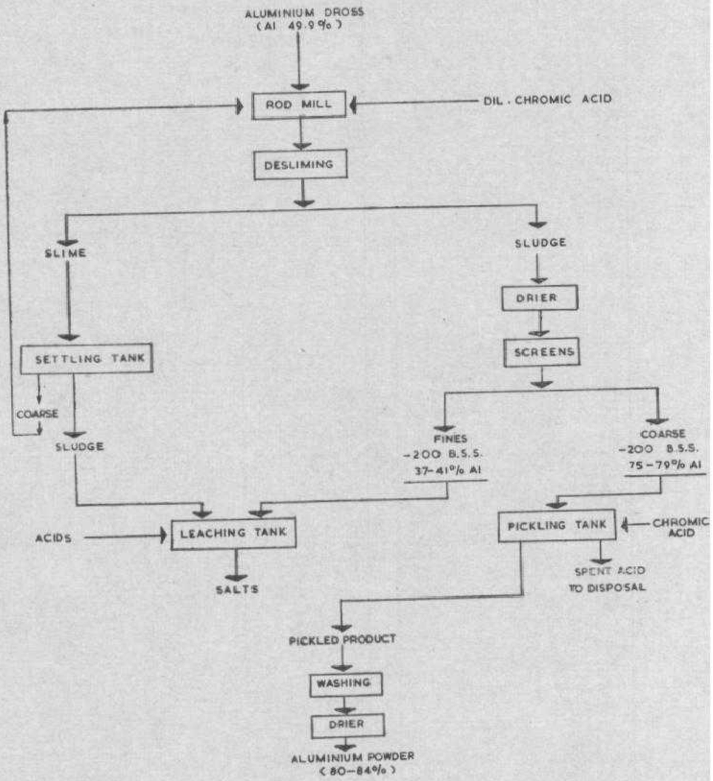
Ashes and skimmings containing both oxides and metallic phases are treated by conventional ore-dressing methods or chemical methods. National Metallurgical Laboratory has carried out considerable work on reclamation of metals from wide varieties of scraps and wastes, both by physical, chemical and pyro-metallurgical methods.

(a) Precious metals from dross : A sample of gold-silver dross,[16] mixture of slag and floor sweepings, it assayed 13·68 dwt gold/ton and 10·8 oz silver/ton and contained slag, graphite and clay as the main constituents. Both tabling and flotation accompanied by cyanidation were tried. Flotation of both gold and graphite at—200 mesh yielded a flotation concentrate assaying 56·32 dwt gold/ton with a recovery of 73·7% gold. Cyanidation of the flotation tailing increased the total recovery of gold to 85%.

(b) Metallics from aluminium dross : A sample of aluminium dross[17] from aluminium melting furnaces assayed 27·7% Al, 43·7% Al_2O_3, 2·07% SiO_2, 4·01% C, 1·05% Fe and 2·3% alkalies. The principal gangue was alumina with small amounts of quartz and graphite. Metallic aluminium was mostly present in rounded grains, generally having a coating of oxide. Electrostatic separation of the ground deslimed sample produced a concentrate assaying 57·3% Al with a recovery of 31·7%. Flotation after grinding the sample to 57%—200 mesh and using oleic acid emulsion and pine oil produced a concentrate (as flotation tailing) assaying 57·4% Al with recovery of 39% Al. Use of more collector and increased flotation time, yielded a flotation tailing assaying 85·67% Al with a recovery of only 10·3%. The recovery in all the tests was low due to the fineness of the metallics which were mostly in the dust float and slime.

A sample of aluminium foundry dross containing 49·9% metallic Al, 22·43% Al as oxide, 0·47% Si. 9·6% SiO_2, 2·2% Fe, 1·9% C, 0·11% Mn, 1·68% Mg, 1·05% Cu, 0·80% CaO and 0·64% alkalies was successfully treated for recovery of aluminium.[18] Various methods investigated include melting of briquetted dross with and without desliming as well as with flux addition, grinding followed by gravity separation, grinding in presence of dilute chromic acid or a mixture of HNO_3, chromic acid, HF or an alkali fluoride in order to remove oxide coating from the metal surface and also for surface brightening.

It was observed that direct melting of dross with or without flux addition resulted in considerable oxidation losses. The heavy proportion of gangue material such as the thick coating of oxide on the metallic surfaces could be removed by grinding and washing. Grinding in presence of chromic acid in a rod mill improved the metallic aluminium content to 79%. Further improvement in the grade was achieved by acid treatment of this product. Based on the investigations, a flow-sheet for upgrading the aluminium dross has been formulated and given in Fig. 8. The recovered aluminium powder can be directly used for thermit reaction and other pyrotechnic applications.

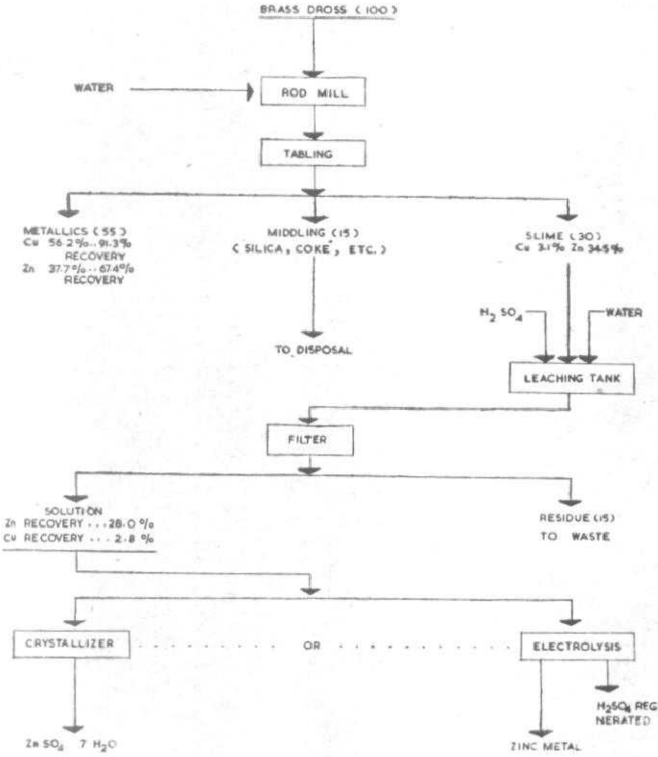


8 *Flowsheet for treating aluminium dross*

(c) Recovery of metallic values from brass dross :

Studies were undertaken for recovery of metallics[19] from a sample of industrial brass dross containing 34·93% copper and 34·46% zinc. Wet grinding of the dross liberated the adhering oxides and facilitated their separation by simple gravity methods. The concentrate analysed 56·2% Cu and 37·7% zinc. The slime containing 3·2% Cu and 34·5% Zn was leached with dilute H_2SO_4 dissolving 70% of zinc, which could be crystallized as $ZnSO_4$, $7H_2O$ or electrolysed. An overall recovery of 95·4% Cu and 94% zinc was recorded. A flow-sheet for the recovery process has been given in Fig. 9 based on experimental results.

(d) Recovery of zinc from galvanizers' dross : Zinc dross formed during galvanizing is essentially a mixture of zinc-iron compounds with entrained zinc. For every 50 000 tons of zinc used for galvanizing, about 12 000 tons of dross is produced, which is not being put to direct use for the recovery of much needed zinc. After reviewing all the possible methods for the recovery of zinc, such as liquation, sweating, filtration, centrifuging,



9 *Flowsheet for treatment of brass dross*

aluminium and modified aluminium process, atmospheric distillation and vacuum distillation, systematic investigations were carried out for atmosphere and vacuum distillation of zinc from dross.[20]

Atmospheric distillation was carried out in ordinary Salamander crucibles without the use of special retorts. Over 90% zinc recovery was attained by carrying out the distillation at 1000–1100°C. Large scale trials were carried out with 40 kg lots of dross containing 3·6% Fe. The distillation unit is schematically shown in Fig. 10. Various factors studied include the temperatures of distillation and condensation as well as the size and inclination of the condenser. Typical experimental data are given below :

Wt. of dross treated (3·6% Fe)	...	40 kg
Wt. of reclaimed zinc	...	35 kg
Temp. of distillation	...	1200°C
Recovery of zinc	...	92%

Owing to the obvious advantages of vacuum distillation, systematic studies were undertaken to study the vacuum distillation of dross and the results of laboratory scale tests carried out for one hour distillation are indicated in Table IV.

TABLE IV Distillation of zinc dross under vacuum

Sl. No.	Temperature of distillation	Pressure in the system (in mm. of mercury)	Weight per cent of residues left undistilled
1	550°C	1·0	9·35
2	600°C	1·0	5·00
3	650°C	1·0	3·60
4	650°C	1·5	4·00

From the distillation experiments, it is evident that the zinc recovery increases with increase in the temperature of distillation. With lower pressures in the system the recovery of zinc increases. From the weight of residues left behind it is evident that metallic zinc can be almost completely recovered.

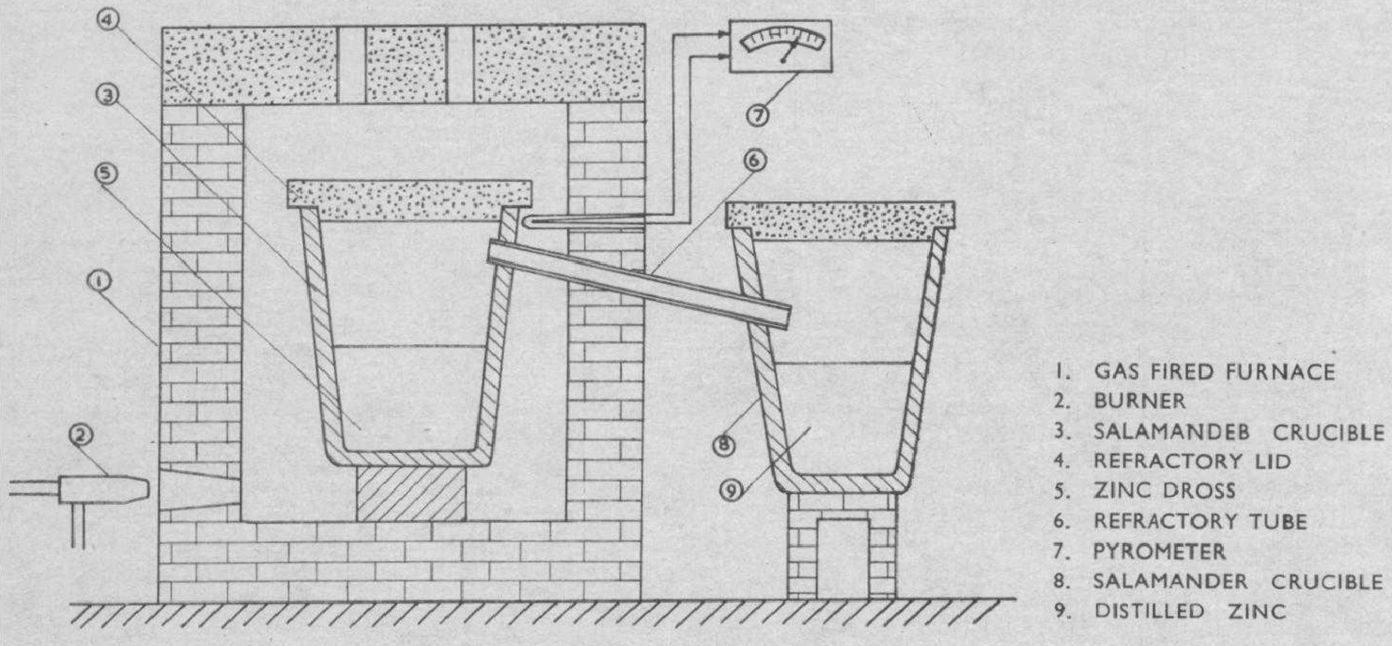
Based on the laboratory scale experiments, a vacuum retort having a capacity to distil 10 kgs zinc dross per batch was designed and fabricated at the National Metallurgical Laboratory. The pot was heated externally inside a gas fired pot furnace, having radiation baffles to protect the rubber gasket and water cooling tubes. A rotary oil sealed vacuum pump was employed for evacuating the system and the pressure was read off from a Mcleod gauge connected to the vacuum line and zinc was distilled at different temperatures.

Results of the experiments carried out with 10 kg charge of zinc dross per batch are indicated in Table V.

TABLE V Results of distillation tests carried out for various periods and temperatures

Experiment No.	Distillation temperature °C	Distillation period (hour)	% Metallic zinc recovery
1	550	3	75
2	600	3	80
3	650	3	85
4	650	1	50
5	650	2	83
6	650	5	98

Optimum conditions were arrived at to recover over 95% zinc from the zinc dross and a pilot plant capable of treating 300 kg of dross is under installation. Development of a continuous zinc distillation unit is also being investigated.



10 *Schematic diagram of atmospheric zinc distillation unit*

Vacuum distillation of zinc ash and skimmings was also attempted and found to be successful by using adequate compacted charge.

Substitution

In addition to the conservation of non-ferrous metals of strategic importance, it is imperative to explore the possibility of replacing the use of scarce metals with those available more abundantly in the country. The only non-ferrous metal for which abundant resources are available in the country is aluminium and it is desirable that extensive efforts should be made to develop the increasing application for this metal. The modest efforts in this direction have already shown promise and it is hoped that with the increased quantities of the metal being available to the industry, its application will increase at a faster rate. Considerable quantity of metallic oxides are being used as pigments and the possibilities of substituting zinc and lead oxide by titanium dioxide, ferric oxides, etc. need important consideration.

(i) Substitution by aluminium

The use of aluminium in increasing quantities and as a major substitution material today is favoured by its outstanding physical properties such as its low density, high strength to weight ratio, corrosion resistance, nontoxic character, high thermal and electrical conductivity, high reflectivity, etc.

The versatile properties of aluminium have already rendered it eminently suitable for a variety of purposes that are finding increasing application. Aluminium utensils and domestic appliances are competing satisfactorily with stainless steel, copper, brass, etc. Aluminium sheets are competing with galvanized sheets for roofing and panelling, aluminised articles can likewise replace galvanized articles. Aluminium foils are increasingly replacing lead, tin, etc. in packaging and canning, 'AAC', 'ACSR' and 'ACAR' cables are replacing copper in electrical conductors particularly in India.

The requirements of aluminium in India by consumer industries as estimated[21] by the Planning Commission are given in Table VI.

TABLE VI Aluminium requirement in consumer industries

	1960–61	1965–66	1970–71
	(in thousand tonnes)		
Transport equipment	2·8	7·0	14·2
Electrical industries	17·1	49·9	88·8
Food/textile and chemical equipment	2·5	5·6	10·0
Building and construction	3·8	6·6	10·0
Canning and packing	4·0	7·5	15·0
Domestic utensils and other commercial supplies	10·0	21·2	42·6
Miscellaneous unspecified uses	4·1	9·8	18·0
Production reserves of consumers and addition to stocks	4·1	12·4	23·4
Exports	—	5·3	15·0
Total	49·0	125·0	237·0

It is thus seen that there is considerable scope for the industry to be expanded manifolds and with the following substitutions suggested the demand will increase manifolds.

(ii) Substitution for copper

Serious efforts are already being made in India for the replacement of copper and its alloys by aluminium.

(i) Replacement of bare copper conductors by aluminium conductors to the extent of 15 000 tons by 1970.

(ii) Substitution of 2 500 miles of paper-insulated cable, based on copper wire by aluminium wire by 1970.

(iii) Substitution of copper by aluminium in heavier VIR and PVC wires to the extent of 600 000 000 yards by 1970.

(iv) Replacement of copper and copper base alloys by aluminium and other alloys for switch gears by about 20% by 1970.

(v) Curtailment of about 50% copper consumption for hardware by substituting aluminium and alloys in its place.

(vi) Substitution of copper and copper base alloy utensils by aluminium.

The extensive use of aluminium in electrical industry to dispense with valuable copper is based on its application as conductor as well as in associated metallic components. The growth of electrical industries and widespread power distribution in India demand huge tonnage of conductors and Aluminium Conductor Steel Reinforced (ACSR) and All Aluminium Conductors (AAC) as well as Aluminium Conductors Aluminium Alloy Reinforced would serve as useful substitutes for this purpose. It has been estimated that for the same current carrying capacity Rs 40/– to Rs 50/– worth of aluminium would replace every Rs 100/– worth of copper and on overall saving of 15–30% can be achieved using cheap modern insulating materials like thermoplastics as cover-alls in complete aluminium cables.

The winding of motors and generators have successfully been accomplished by the use of aluminium. The use of aluminium for casting frames in motors such as in electric fan industries in addition to its use in fan blades and other die-cast end frames will result in cost reduction as well as better performance due to weight saving which will compete better in foreign market. The fairly well-established application of transformer windings with aluminium should also be considered for its application in such directions in India.

Copper can be replaced by aluminium in other electrical applications such as in lamp caps, capacitor-cans, lamp holders, bus-bars in electro-plating and allied applications, etc. and such replacements would save considerable amount of copper for more essential uses.

In the field of cryogenic applications aluminium is replacing copper in air-conditioning and refrigerator units. Chromium-plated brass can be efficiently replaced by aluminium roll bonded sheet which is now manufactured indigenously and the manufacturers of refrigerators and water coolers should switch on to the latter.

Considerable tonnage of copper and brass is being consumed for hardwares such as door hinges, handles, aldrops, racks, hangers, sanitary fittings and fixtures including screens, nuts and bolts, etc. which could be made out of steel or aluminium alloys. It has been estimated that 280 tons of copper was used for making zip fasteners in 1960 and increased to 600 tons in 1965–66. Aluminium alloys are quite satisfactory for such applications and such alloys should be made indigenously.

Use of aluminium for coinage is already practised in some countries like France and more recently in India. The replacement of copper for one paise coins only would save 3 000 tons of copper and use 900 to 1 000 tons of aluminium for the purpose. The recent introduction of two and three paise Al-Mg coins has also resulted in considerable saving of copper and nickel.

(iii) Substitution for zinc

Serious shortage of imported zinc in the country has adversely affected the galvanizing industry and an all-out effort is being made to conserve and reclaim zinc from all metallurgical wastes. Besides reclaiming zinc from all the waste products of the galvanizing industry, serious efforts have to be made to commercially adopt the aluminizing process developed at the National Metallurgical Laboratory owing to the manifold advantage of the latter.

The merits of aluminizing over galvanizing have to be judged not only from its better over-all surface protection, but also due to the non-availability of sufficient quantities of indigenous zinc. The aluminized products have greater resistance to normal atmospheric corrosion, including highly humid and sulphurous atmospheres, greater heat resisting properties, better finish of the end material by light cold rolling etc. Due to good scaling resistance at room temperature to a good range of elevated temperature, it can be used for automobile parts such as manifold pipes, mufflers for carburizing boxes, etc. Aluminium-coated cast iron can be used for oven lining, hangers, conveyor parts, enamelling racks, furnace parts, thermocouple protection sheaths, gate bars, heaters and radiators, etc. and all these speak of the supremacy of aluminizing over galvanizing. In view of the obvious advantages of aluminizing over galvanizing for multifarious applications, it is strongly felt that as far as possible galvanizing should be disarrayed in favour of aluminizing.

Substitution of brass wares in various electrical as well as hardware and domestic appliances by aluminium also saves considerable proportion of zinc. Advantages for zinc die-casting alloys are due to their greater dimensional accuracy (0·05 mm/100 mm compared to 0·1 mm for Cu), longer die life (more than 2 to 50 times of Al alloys), small draft angle, finer and more easily maintained core pins, lower injection pressure (60–150 kg/cm^2 against 500–900 kg/cm^2), negligible solution in iron, lower casting temperature, etc. On the other hand, Al alloys are cheaper, have high strength at temperatures above 100°C, high thermal and electrical conductivities and where complexity are concerned aluminium can compete with the best zinc die-casting alloy (Zamak) for castings heavier than 300 gms. Development of aluminium base die-casting alloys would gradually replace zinc die-casting alloys and substantial progress has already been made throughout the world.

(iv) Substitution for tin

The scarcity of tin is felt not only in India but it is prevailing all over the world. The world consumption for tin today has reached 180 000 tonnes annually, whilst with the present production capacity the present stockpile is expected to be exhausted by 1969 and the demand at the present level cannot be met resulting in inevitable price rise. Serious efforts are being made all over the world to substitute tin.

Nearly 50% of the world's demand for tin is by the tin plate industry and the rest for alloying e.g. in solders, white metal bearing alloys, low melting alloys, etc. Substitution of tinned cans by aluminium or plastics, lacquers, coatings, should be investigated. Dry packaging by aluminium of food materials such as dried vegetables, tea, tobacco, etc. have already been successfully adopted in India. Use of aluminium as canning material has rapidly increased in U.S.A., for a wide variety of commodities, e.g. frozen juice concentrate, motor oil, aerosols, bear cans, bear lids, tuna and other drawn cans. Though aluminium can replace tin in most of the dry cannings, it is not a good material for canning acid fruits, tomatoes, tomato sauces and pickles containing acetic acid. Brine used for canning peas etc. attacks aluminium ordinarily but alloys with 1 to 6% magnesium can be used successfully for such storage.

Alloys of aluminium used in canning are, Al (99·8–99·5%) for fish packing, Al (98%) of commercial purity, Al-Mn alloys (1·25% Mn), Al-Mg alloys (1–6% Mg). The corrosion resistance of all these alloys can be increased by anodising and decorative printing is also possible.

During the last World War serious shortage of tin prompted the adoption of emergency specifications. Use of 60% Sn-alloys were brought down to 20% Sn-alloys and similar curtailment of usage of tin would result 50% saving in tin. The railway and automotive industry should be persuaded to try to use aluminium bearing alloys developed recently, some of which are technically superior to bronze bearings. S.G. iron has also been used to replace railway carriage wagon bronze bearings and aluminium bearings are being produced in the country.

Use of solder in the growing electronic industry is bound to consume a sizeable proportion of tin and the use of 60–40 solder instead of 50 : 50 grade would help to some extent in conservation of tin.

(v) Substitution for lead

The present Indian lead smelter produces only 3 600 tons of refined lead annually, though the present demand is 67 000 tons and is expected to increase to 145 000 tons by 1970–71 and to 220 000 tons by 1975–76. The shortfalls can only be met by increasing the production capacity and substitution of lead by other metals wherever possible, so that the lead may be conserved for such essential uses like atomic energy applications, storage batteries, etc.

The primary use of lead is in sheathing to protect against corrosion and with the increased use of acid resisting plastics and cements a substantial saving of lead can be effected. Power distribution underground cables need lead sheathing and use of aluminium conductors as substitute for copper being thicker, requires larger proportion of lead. It is estimated that when one ton of aluminium displaces 2 to 2·5 tonnes of copper, it adds a ton of usage of lead as sheathing. However, aluminium can also be used for sheathing to replace lead and a ton of aluminium would then replace 5 to 6 tons of lead as sheathing material. On the whole, substitution of aluminium for copper in power cables also warrants substitution of lead by aluminium in the sheathing, thereby saving weight and cost simultaneously. Plumbing consumes a considerable quantity of lead which can be substituted by plastics.

Lead base pigments such as red-lead can easily be replaced by aluminium paints or iron oxide paints and this aspect needs scrutiny.

A significant proportion of lead is consumed for storage batteries which is hard to replace. The other alternatives such as nickel-cadmium cells are far too costly and these metals are still scarcer. Research efforts in this light may prove helpful but require both time and patience.

White lead which is used presently for painting can be replaced by titania pigments. Increased use of lead tetra-ethyl as peroleum additive would consume substantial tonnage of metallic lead with the ever increasing automobile industries. Provision should be made for the use of lead in this respect which is unavoidable. Nevertheless, research should be directed to find a substitute for such additives.

(vi) Substitution for nickel

Nickel is mainly used for stainless steels, electro-plating, high nickel heat and corrosion resisting alloys, constructional alloy steels, copper and brass products as well as coinage alloys, the relative extent of their worldwise application being in the order indicated above. Some of the interesting developments of use of nickel in India in recent years are Ni-hard liners Type I and Type IV in cement industry for abrasion and wear resistant applications. A substantial quantity of nickel is also used for coinage in India. In the authors' opinion the use of nickel and nickel-bearing stainless steels has to be made judiciously as the entire indigenous requirement of this metal is based on imports alone. Development of nickel-free stainless steel at the

National Metallurgical Laboratory is a big leap forward in displacing the nickel-bearing stainless steel and its manufacture in the forthcoming alloy-steel plant would definitely ease the nickel consumption in the country.

The Ni-hard liners used in cement industries can be replaced by manganese steels of Hadfield type which would give higher wear resisting properties.

Use of nickel in the plating industries is primarily based on the ease with which the operation is carried out. But chromium plating can be used successfully to give better corrosion resistance to the surface coating as well as the desired finish in the product. In view of sufficient occurrences of chrome ores in the country for manufacture of chromium chemicals, the more costly nickel-plating should be replaced by chromium in electro-plating industries.

The development of nickel-free heating elements is yet another effort by the National Metallurgical Laboratory to develop substitute materials.

(*vii*) *Prospects of moulded plastics*

Though not a member of metallic family, plastics have proved to be highly competitive material to substitute metals in modern markets. The wide varieties of plastic materials are substituted in domestic electrical appliances, hardwares, automobiles, packaging, surface coating, etc. Fibre glass reinforced polyster resins even compete with some grey cast irons.

The plastic substitutes are advantageously used owing to their low price, chemical resistance, colour, attractive surfaces, better heat and electrical insulation properties, sound damping characteristics, durability, etc. Though their production cycle is slow, the production is very regular and completely automatic ; they provide scope for placing inserts, reduced trimming costs, less maintenance cost as well as accuracy in size and shape. With these advantages they have displaced metallic counterparts and should continue to do so in India where the primary use remains in toy making or domestic ware.

While plastics continue to compete with metals in the present world, they have limitations as they are not heat resistant, have poor mechanical properties, lower rigidity, low strength above 110°C, poor dimensional stabilities with time and usage or on moderate heating, low hardness and high coefficient of thermal expansions.

For a metallurgist today, in the face of emergency and countrywide support for self-sufficiency, as much attention is to be paid for speeding up metal production targets and their conservation, as it is for the possible substitution of the scarcer metals by a readily available metal or non-metal. For low temperature applications, plastics do have an important role in displacing metals of strategic importance.

(*viii*) *Revision of standards*

Revision of Indian Standards, at least on temporary basis, is necessary with the possible consideration of substitutes for strategic metals. This will have a direct bearing on minimising the use of virgin metals leading to their conservation and subsequent minimisation of foreign exchange drainage. The Indian Standards Institution has already constituted a Committee on the revision of the Indian Standards. The example for such revisions are numerous and stagewise introduction of new standards is desirable so as to enforce them more or less permanently in view of the country's resources and their exploitation.

Conclusion

Conservation and substitution of scarce materials is the basic necessity of the country in view of the serious shortage of foreign exchange. Metallurgists have their prominent part to play to help the nation out of the present crisis by serious thinking and judicious appraisal of the country's needs in their field. Conservation as well as substitution are not as easy as it appears to be and a considerable effort has to be made in educating the people—consumers as much as the manufacturers. Continuous and repeated persuasion is necessary to remove the popular conservation outlook, effective publicity mechanisms are to be evolved out, and finally resort has also to be taken in legislative measures so as to implement the application of possible substitution materials in place of the age-old use of scarcer metals.

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