VACUUM — A NEW TOOL IN EXTRACTIVE METALLURGY

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Abstract

Theoretical considerations involved in metal extraction reactions under vacuum have been discussed. The general advantages of carrying out reactions under vacuum are derived from the lowered temperature for reaction and the possibility of carrying reactions to completion, by the removal of one of the reaction products.

The conditions for the reduction and dissociation of oxides, sulphides, halides, hydrides and nitrides are discussed and various examples cited of reactions of this type adopted for metal-winning.

Introduction

VACUUM technique found its first large-scale industrial application in the metallurgical field as early as World War I when Rohn[1] in Germany made its use to degas and purify metals and alloys. A later development was the distillation of metals and alloys under vacuum. This offered one of the most effective methods for refining metals and opened fresh avenues for the treatment of reactive metals. For some years, however, vacuum distillation found little industrial application excepting for the purification of mercury[2] and the removal of zinc from lead[3]. At that time and earlier various workers[4-18], however, mentioned about the purification of magnesium, chromium and manganese by vacuum distillation.

During World War II new openings for vacuum metallurgy were found and the technique was successfully employed for the production of magnesium by the reduction of magnesia and dolomite by ferro-silicon. A large-scale application of vacuum technique has recently been reported in the production of low-carbon ferrochrome[19].

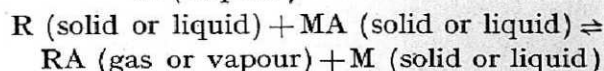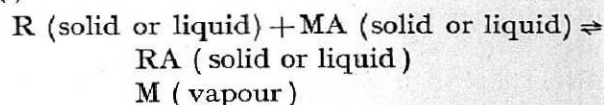Vacuum methods offer new and varied opportunities in the field of pyrometallurgy.

Amongst such applications may be mentioned the extraction of metals, recovery of metals, melting of reactive metals, decarburizing, deoxidation and heat treatment.

This paper deals in outline with the principles and theoretical considerations involved in carrying out metal-winning reactions and allied processes under vacuum.
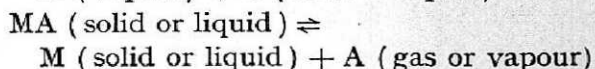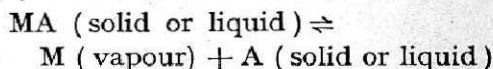
Theoretical Considerations Involved

The reactions that are favoured by vacuum have been classified by Stauffer[20] and may be represented as follows:
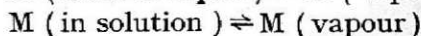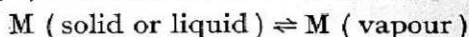
(i) *Thermal Reduction* —

R (solid or liquid) $+$ MA (solid or liquid) $\rightleftharpoons$
    RA (solid or liquid)
    M (vapour)

R (solid or liquid) $+$ MA (solid or liquid) $\rightleftharpoons$
    RA (gas or vapour) $+$ M (solid or liquid)

(ii) *Thermal Dissociation* —

MA (solid or liquid) $\rightleftharpoons$
    M (vapour) $+$ A (solid or liquid)

MA (solid or liquid) $\rightleftharpoons$
    M (solid or liquid) $+$ A (gas or vapour)

(iii) *Sublimation or Distillation* —

M (solid or liquid) $\rightleftharpoons$ M (vapour)

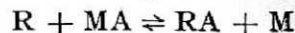M (in solution) $\rightleftharpoons$ M (vapour)

where

    R $=$ Reducing agent;

    M $=$ Metal;

    A $=$ Acid radical, e.g. sulphur, oxygen, etc.

The above reactions are similar in that they involve solid or liquid reactants and gaseous reaction products. The theoretical considerations for each type of reaction are given below:

(1) *Thermal Reduction* — The reduction reactions have been expressed as:

$$R + MA \rightleftharpoons RA + M$$

It is well known that any such reaction is reversible and provided the compounds on both sides remain in the same phase and are not removed a balance is soon set up. The equilibrium will, however, be upset and the reaction driven to one side by removal of one of the products preventing the back reaction. Use of vacuum helps to eliminate one of the volatile reaction products, whether the metal or the other product, thus driving the reaction to completion.

In certain cases though free-energy data may not favour the reaction at a particular temperature at atmospheric pressure, the pressure in the system may play a decisive role by changing the free-energy temperature relationship; it is then possible to carry reaction at a low temperature under vacuum. Fig. 1 shows the change in free energy for the reaction $2Mg + O_2 = 2MgO$ under reduced pressures. It is seen that magnesia might be expected to react with silicon at a pressure of 0·01 mm. at about 1650°C. At atmospheric pressure, however, no reaction would be possible at this temperature.
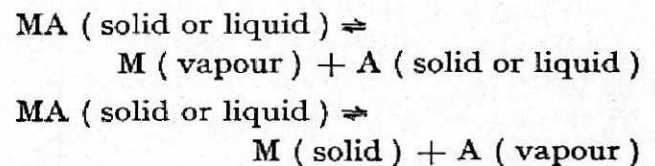
Various theories have been suggested for the initiation of the type of reactions when

FIG. 1 — FREE ENERGY DIAGRAM SHOWING THE EFFECT OF REDUCED PRESSURE

MA is in the solid state at the temperature of reaction. The mechanism of reaction involved in the Pidgeon process for producing magnesium has been investigated by several workers. The reaction is represented as:

$$2MgO \cdot 2CaO + Si(Fe) \rightleftharpoons$$
$$2CaO \cdot SiO_2 + 2Mg + Fe$$
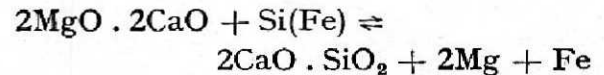
It was at first suggested that the reaction took place between a vapour phase and magnesium oxide, the vapour phase being either Si or SiO. Pidgeon[21] subsequently proved that the reaction was due to solid diffusion between the reactants of the system.

(2) *Thermal Dissociation* — The general type of reaction representing thermal decomposition may be represented as:

MA (solid or liquid) $\rightleftharpoons$
M (vapour) + A (solid or liquid)
MA (solid or liquid) $\rightleftharpoons$
M (solid) + A (vapour)

In the above type of reaction an equilibrium is set up when the partial vapour pressure is equivalent to the dissociation pressure. However, by lowering the partial pressure over the system until it is less than the equilibrium dissociation pressure the decomposition will almost go to completion. The dissociation pressure is given by the relationship:

$$\log p = A - \frac{B}{T}$$

where A and B are constants.

The equilibrium pressure thus decreases with increase of temperature. Dissociation or decomposition may be carried out at much lower temperature under vacuum. Another advantage of carrying out the reaction under vacuum is that contamination from the air is avoided, thus yielding purer products.

Dissociation can only be applied to metal-winning if the equilibrium dissociation pressure is high. The compounds of interest to metallurgists are the oxides, sulphides, halides, nitrides, hydrides, etc. The dissociation
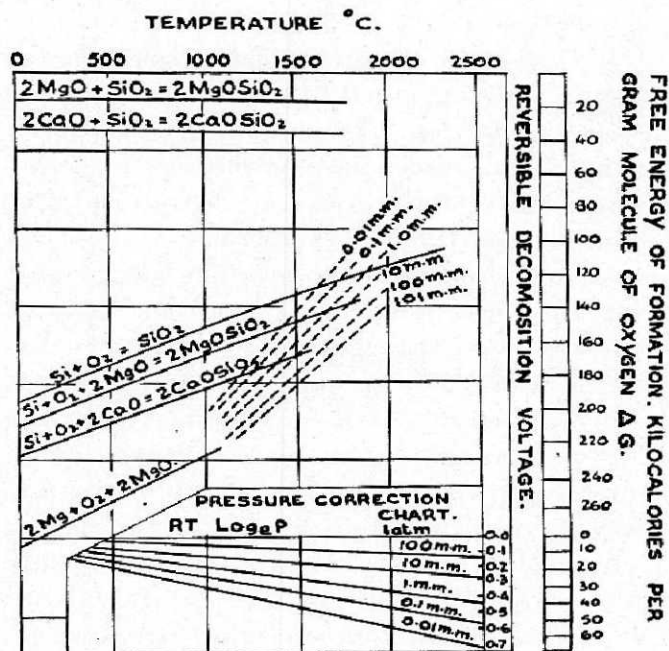
of sulphate or carbonates may also be applied for the preparation of pure oxides.

(3) *Sublimation or Distillation* — As already pointed out, evaporation pressure may be expressed by the relationship

$$\log p = A - \frac{B}{T}$$

Due to the logarithmic character of the equation, considerable decrease in the operating temperature for evaporation can be effected by working under low pressures. In view of the higher hydrostatic pressure, boiling from liquid metals is more of a surface phenomenon under vacuum. Accordingly, for evaporating a metal rapidly in a vacuum, a maximum boiling surface is desired.

The vapour pressure of a metal at its triple point indicates the temperature at which the metal can be sublimed or distilled. Kroll[22] showed that distillation or sublimation can be carried out on a commercial scale only at a vapour pressure of above 1·8 mm. The success of the process would depend if this vapour pressure is within the range of working temperature. If the temperature at which the vapour pressure is 1·8 mm. falls below the temperature of the triple point, the metal can be vaporized from solid state at a sufficiently fast rate without melting.

Table 1, compiled by Kroll[22], shows the vapour pressure data at the triple point. The triple point temperature has been determined by Van Arkel and vapour pressure data by Cospe and Kroll[23].

Besides refining metals by distillation, the principle has also been used for refining and separating inorganic compounds of metallurgical interest, e.g. separating mixed sulphides, removal of magnesium chloride and magnesium from titanium after the reduction of titanium tetrachloride with magnesium.

Applications

Vacuum technique may be used at a variety of stages during the process of metal-winning. The various stages at which the

TABLE 1 — VAPOUR PRESSURE AT THE TRIPLE POINT

ELEMENT	TRIPLE POINT, °C.	VAPOUR PRESSURE, mm. Hg
Be	1300	0·1
Mg	650	2·5
Ca	850	1·8
Sr	770	2·0
Ba	710	0·08
Cr	1920	60·0
Mn	1244	0·8
Fe	1535	0·05
Ni	1455	0·01
Cu	1084	0·00061
Ag	960·50	0·002
Zn	419·42	0·1
Cd	302·90	0·05
Sn	232	Negligible
Pb	327·40	,,

application of vacuum has been made may be classified as:

1. Preparation of inorganic compounds, the compounds so produced to be used for metal-winning.
2. Dissociation and reduction of the compounds to produce the metal.
3. Refining metallic reaction products by distillation.

The use of vacuum as an aid for metal-winning was suggested by Guntz[24] and in fact they produced barium and strontium by reducing their oxides in vacuum with aluminium. Matignon[25] later on introduced and recommended the use of silicon. Silicon was also used by Matignon to produce magnesium from calcined dolomite. Another reaction suggested was the reduction of magnesium chloride with calcium carbide, but this could not be applied in practice as no heat-resisting steels were available during World War I[26,27].

The following enumerates reactions that are being practised or offer possibilities in metal-winning. It may be mentioned that many other reactions may also be suitable under vacuum and may offer certain advantages over established or conventional methods, but the cost involved in adopting the vacuum

technique may be prohibitive. The application of vacuum to metal extraction is possible only in those cases where definite economic advantages are afforded.

Preparation of Inorganic Compounds — As in metal-winning reactions, suitable inorganic compounds may be prepared under vacuum either by dissociation reaction, double decomposition or distillation.

The usual advantages offered by carrying out such reactions under reduced pressure are that the reaction can, under such condition, be carried out at a lower temperature and that the reaction products are much purer.

(a) *Dissociation reactions* — Oxides are the only inorganic compounds that are formed by dissociation and subsequently used for metal-winning.

The compounds of commercial interest that may be dissociated into oxides are sulphites, sulphates and carbonates, and occasionally oxalates.

The dissociation pressure of various inorganic compounds compiled by Kroll is given in Table 2.

The only instance of immediate industrial interest is Li_2CO_3 as no particular advantage is served by carrying out the reaction under reduced pressure in other cases. The lithium oxide produced by vacuum decomposition of the carbonate is very pure and is used for subsequent reduction to metal.

TABLE 2

COMPOUND	TEMPERATURE, °C.	DISSOCIATION PRESSURE, mm. Hg
SrCO₃	809	3·6
BaCO₃	824	8·6
	600	1·8
CaCO₃	650	6·9
	700	22·0
	897	760·0
Na₂CO₃	990	12·0
K₂CO₃	1300	15·1
Li₂CO₃	723	4·0
MgSO₄	950	24·0
CaSO₄	1000	1·3
FeO	1073	$6·3 \times 10^{-12}$

(b) *Double decomposition* — Other reactions which offer possibilities for making inorganic compounds suitable for subsequent metallurgical treatments may be mentioned as follows:

Beryl ore may be directly treated in vacuum at 1000°C. with aluminium or magnesium fluorides, and the beryllium fluoride so produced distilled out[28].

Clay reacts with sodium fluoride under vacuum producing sodium aluminate and silicon fluoride. Aluminium fluoride and calcium aluminate are formed when it reacts with calcium fluoride[29].

A reaction between copper sulphide and cuprous oxide can be performed at low temperature under reduced pressure.

The low vapour pressure of magnesium fluoride could be the basis of the following type of reaction:

$$MgCl_2 + XF_2 \rightarrow XCl_2 + MgF_2$$

(c) *Distillation or sublimation of inorganic compounds* — Differences in the vapour of compounds may be used as a means of separating the mixture by selective volatilization. This has found commercial application in the separation of lead and cadmium sulphides from zinc calcines.

Dissociation and Reduction of the Compounds to Produce the Metal — The theoretical considerations for dissociation and reduction have already been discussed. The compounds that may be of use in metal-winning by dissociation and reduction include oxides, sulphides, halides, hydrides and nitrides. The behaviour of each of these types is considered separately.

Dissociation and reduction of oxides — The volatility of most metallic oxides at high temperature seems to be dependent on the formation of metal and oxygen, or metal sub-oxide and oxygen, or it may be volatilizing without decomposition.

Lead, molybdenum and aluminium oxides fall in the first category and vaporize without decomposition, whilst mercury, cadmium, zinc, magnesium and alkali metal oxides decompose

to the gaseous metal on heating. Silicon and tin decompose with formation of sub-oxides.

All oxides, excepting those of silver and mercury that decompose on heating, have too low a dissociation pressure to be of any help in metal-winning. Table 3 shows the dissociation pressures of some of the decomposable oxides.
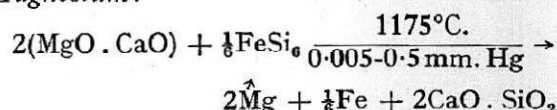
TABLE 3

CdO $\log_{10} P = \dfrac{-13100}{T} + 7 \cdot 920$

ZnO $\log_{10} P = \dfrac{-16173}{T} + 6 \cdot 760$

CaO $\log_{10} P = \dfrac{-26605}{T} + 6 \cdot 530$

MgO $\log_{10} P = \dfrac{-26173}{T} + 8 \cdot 040$

HgO $\log_{10} P = \dfrac{-5227}{T} + 7 \cdot 430$

Ag_2O $\log_{10} P = \dfrac{-2859}{T} + 9 \cdot 166$

PdO $\log_{10} P = \dfrac{-10230}{T} + 11 \cdot 860$

It is clear from the above relationship that thermal decomposition of oxides does not offer possibilities for the extraction of metal. First, very high vacuum and temperature would be necessary for the decomposition excepting in the cases of mercury and silver, and, secondly, even if decomposition occurred (at the cost of high temperature and vacuum), the problem of back reaction would be very serious as both the reaction products being in gaseous form would evacuate out.

The reduction of oxides has, however, been carried out successfully under vacuum at comparatively low temperature. The reaction may be conducted for producing either volatile or non-volatile metals.

Volatile metals — The Pidgeon process for the reduction of dolomite to magnesium has been one of the foremost in vacuum metallurgy in terms of quantity produced. The reduction at the temperature and pressure involved may be expressed as:
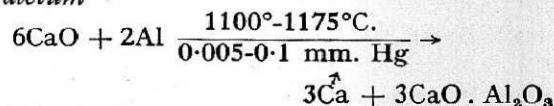
Magnesium:

$$2(MgO \cdot CaO) + \tfrac{1}{6}FeSi_6 \xrightarrow[\text{0·005-0·5 mm. Hg}]{1175°C.} 2\overset{\uparrow}{Mg} + \tfrac{1}{6}Fe + 2CaO \cdot SiO_2$$

It is estimated that between 1941 and 1945 over one hundred million pounds of magnesium were produced in America[31] by this method. Most of the plants in U.S.A. producing magnesium by this process were, however, shut down at the conclusion of the war. This has been attributed by Stauffer[20] mainly to poor plant locations and abnormally high capital investment rather than the inherent high cost of the method. Dominion Magnesium Ltd. in Canada has been reported to be still producing magnesium and calcium by this method.
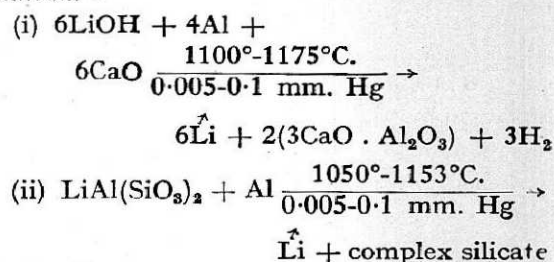
Barium and saesium have also been produced commercially by vacuum thermal reduction.

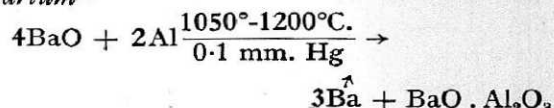Other reactions that have been reported as having been investigated are:

Calcium[31,32]

$$6CaO + 2Al \xrightarrow[\text{0·005-0·1 mm. Hg}]{1100°-1175°C.} 3\overset{\uparrow}{Ca} + 3CaO \cdot Al_2O_3$$

Lithium[33,34]

(i) $6LiOH + 4Al +$
$$6CaO \xrightarrow[\text{0·005-0·1 mm. Hg}]{1100°-1175°C.} 6\overset{\uparrow}{Li} + 2(3CaO \cdot Al_2O_3) + 3H_2$$

(ii) $LiAl(SiO_3)_2 + Al \xrightarrow[\text{0·005-0·1 mm. Hg}]{1050°-1153°C.}$
$$\overset{\uparrow}{Li} + \text{complex silicate}$$

Barium[35]

$$4BaO + 2Al \xrightarrow[\text{0·1 mm. Hg}]{1050°-1200°C.} 3\overset{\uparrow}{Ba} + BaO \cdot Al_2O_3$$

Additionally, it is possible to reduce the oxides of other volatile metals such as lead, zinc, manganese and bismuth with silicon under vacuum, but the standard methods are much cheaper.

Non-volatile metals — In the reduction of oxides of non-volatile metals the reaction is

carried to completion by driving off a gaseous byproduct by vacuum.

Columbium has been reported to have been produced by the reaction of columbium oxide and columbium carbide[36] under vacuum.

$$Cb_2O_5 + 5CbC — 7Cb + 5CO$$
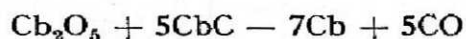
Tantalum oxide can be reduced to the metal by silicon under vacuum[37]. Silicon forms the monoxide which is volatilized away.
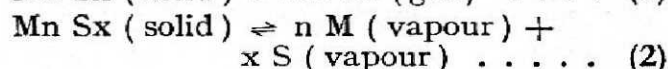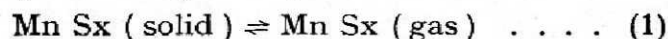
Schlecton and Kroll[38] showed the possibilities of thermal reduction of many oxides *in vacuo* with carbon and produced 97 per cent chromium metal and 93 per cent vanadium by the vacuum reduction of their respective oxides.

The type of reaction where the metal is non-volatile and remains behind suffers from the inherent defect that it is difficult to get intimate contact between all the reactants. In certain cases it may even be necessary to remove the charge after partial reduction, crush, re-mix and then resume the operation. Furthermore, another disadvantage is that carbides are invariably formed and mixtures of metal and carbide are left. In these cases complete reduction is not effected because the proportion going to $CO + CO_2$ cannot be predicted. The optimum quantity of carbon must be determined by trial and error. It would not be safe to conclude that carbon or silicon reduction in vacuum has no commercial prospects at present since no comprehensive study of the subject has so far been made.

Dissociation and reduction of sulphides — The principles involved in the vacuum dissociation and reduction of sulphides are similar to those of oxides, i.e. (a) a sulphide having high dissociation pressure may be decomposed into sulphur and metal or (b) a sulphide may be reduced under vacuum with another suitable metal producing volatile metal and non-volatile sulphide or vice versa.

Besides the advantages of carrying out the reactions under vacuum, another advantage is that the sulphides under these conditions are prevented from oxidation.

The possible modes of decomposition of sulphides may be represented as:

$$Mn Sx \text{ (solid)} \rightleftharpoons Mn Sx \text{ (gas)} \quad \ldots \ldots \quad (1)$$
$$Mn Sx \text{ (solid)} \rightleftharpoons n M \text{ (vapour)} +$$
$$x S \text{ (vapour)} \quad \ldots \ldots \quad (2)$$

Between these two cases are others where the sulphide may be partially evaporated as much and partially decomposed.

Schlecton[39] determined the vapour pressure relationship of the volatile and non-volatile sulphides. These are given in Table 4.

In the case of Cu_2S, the dissociation pressure relationship does not follow the pattern of other sulphides and the logarithm of k log p versus $\frac{1}{T}$ is not a straight line. Dissociation pressure (log P mm.) varies from -5.04 to -4.54, from 604° to 906°C. This behaviour has been explained as being due to the formation of fine metallic copper wool on the

TABLE 4

### VOLATILE SULPHIDES
(*P shows the vapour pressure*)

ZnS   log P mm. $= \dfrac{-13981}{T} + 8.979$

CdS   log P mm. $= \dfrac{-10500}{T} + 7.572$

HgS   log P mm. $= \dfrac{-5586}{T} + 6.669$

PbS   log P mm. $= \dfrac{-11160}{T} + 9.338$

SnS   log P mm. $= \dfrac{-8380}{T} + 6.728$

AS_2S_3 log P mm. $= \dfrac{-5098}{T} + 4.672$

Sb_2S_3 log P mm. $= \dfrac{-7674}{T} + 6.764$

NON-VOLATILE SULPHIDES

MnS   log P mm. $= \dfrac{-11937}{T} + 4.633$

FeS   log P mm. $= \dfrac{-10850}{T} + 4.162$

CoS   log P mm. $= \dfrac{-12630}{T} + 6.751$

NiS   log P mm. $= \dfrac{-9213}{T} + 5.840$

MoS_2 log P mm. $= \dfrac{-13839}{T} + 6.678$

surface of sulphide which prevents the escape of vapour.

The reduction of zinc sulphide with iron has been suggested[40,41] by many workers.

$$Fe + ZnS \text{ (solid)} \xrightarrow[\text{1 mm. Hg}]{\text{1000°C.}} FeS + \overset{\uparrow}{Zn}$$
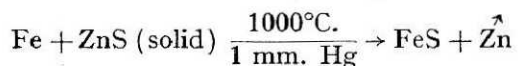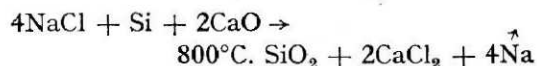
The reaction offers interesting possibilities as stages of roasting and carbon reduction are avoided and the metal is produced in one stage. However, at the high reaction temperature under reduced pressure a certain amount of zinc sulphide volatilizes. It is not yet known if it is possible to condense lead and cadmium selectively. Any noble metals present would be left in the residue and would have to be separated from the sulphides of iron.

Various other sulphides, e.g. those of lead and mercury, could be reduced with iron under vacuum. These, however, do not offer any advantages over well-established processes and none of these suggestions have materialized. Dissociation of molybdenum sulphide offers possibilities for making the metal but would require detailed studies.
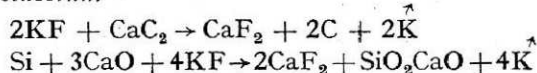
Dissociation and reduction of halides — Most of the halides, excepting fluorides, have high vapour pressure and volatilize without decomposition on heating under vacuum.

The reduction of chlorides for making highly reactive and volatile alkali metals like sodium, potassium, rubidium and caesium has been carried out.

Sodium[42]

$$4NaCl + Si + 2CaO \rightarrow$$
$$\qquad 800°C. \ SiO_2 + 2CaCl_2 + 4\overset{\uparrow}{Na}$$

Potassium[43]

$$2KF + CaC_2 \rightarrow CaF_2 + 2C + 2\overset{\uparrow}{K}$$
$$Si + 3CaO + 4KF \rightarrow 2CaF_2 + SiO_2CaO + 4\overset{\uparrow}{K}$$

Caesium and rubidium can be reduced from their chlorides under vacuum in small quantities, calcium being used as a reducing agent. The reaction is carried out in a glass vessel.

Use of calcium carbide for reduction of lead and zinc chloride has also been suggested.

Excepting the reduction of alkali metal chlorides, the reduction of chlorides in vacuum does not offer any particular advantage over the established methods and has not been put in practice. The reduction of titanium and zirconium tetrachloride is generally effected under an inert atmosphere. The use of vacuum has also been mentioned in both the cases, but it does not offer any advantage over the inert atmosphere.

Many halides can be dissociated by heating to high temperatures. But these reactions cannot be carried to completion as most halides are themselves volatile and are removed along with the halogen.

Dissociation of hydrides and nitrides — The dissociation of nitrides and hydrides is not of much importance so far as the extraction of metals is concerned. The hydrides are important as getters or clean-up reagents and are generally prepared by passing hydrogen over the heated metal. At higher temperatures, the hydride decomposes into the metal and the hydrogen. The formation of hydrides and its dissociation have been applied for the preparation of titanium. The reaction may be represented as:

$$TiO_2 + 2CaH_2 \rightarrow TiH_4 + 2CaO$$
$$TiH_4 \rightarrow Ti + 2H_2$$
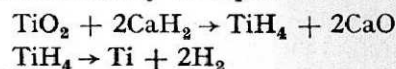
The nitrides are generally very stable and are prepared by heating the metal with nitrogen or ammonia. The nitrides are also prepared by heating the oxide with carbon in an atmosphere of nitrogen at 1200°C. TiN, VN, SiN, LaN, ScN, CbN and CeN are prepared by this method.

The nitrides of chromium, iron and manganese decompose at comparatively low temperature, but do not offer any special advantages in metal-winning.

Refining Reaction Products by Distillation

If the products of a reaction mixture have an appreciable difference in the effective vapour pressure, it is possible to make a separation by distillation. The distillation

will proceed at a lower temperature under vacuum and protect the metal from oxidation.

This has found application in the titanium and zirconium metallurgy[44] where the sponge is purified from magnesium and magnesium chloride by vacuum distillation. Another advantage of vacuum distillation over leaching is that the product is very suitable for sintering and free of all hydrolysed products that may form during leaching.

In the fusion electrolysis of chlorides, the electrolyte is frequently entrapped in the metal dendrites. Vacuum distillation is used for refining the metal. Calcium produced by electrolysis of calcium chloride has been refined by this method[45].

Plant Materials, Furnaces and Pumping Equipment — Operational temperatures for vacuum operations are limited to 1200°C. as no suitable material has been found that will stand higher temperatures under vacuum. Iron retorts are attacked by atmospheric oxidation, but are protected by stainless steel or aluminium up to 700°C. At higher temperature iron has to be protected by a sheath of inconel.

The outside attack on the reaction chamber may be prevented by putting the vessel in an evacuated furnace. Another factor to be considered is the chemical attack of the reaction products within the chamber. Graphite can be employed as a crucible material, but it reacts with almost all refractories and oxides above 1300°C. and gases formed as a result of the reaction may have an adverse effect on the process.

The furnaces used are generally of the electric resistance type, graphite, tungsten, molybdenum, etc., being used as heating elements. Where higher melting temperatures are needed, either high frequency or arc furnaces are used.

For creating the vacuum, mechanical pumps and oil diffusion pumps are used.

Conclusions

The study reveals a number of possible applications in extractive metallurgy, though only a few processes have been established firmly. The main reason may be that vacuum methods are rather new and have not been used in universal scale. The vacuum pumps, valves, etc., for the size and capacity required have only been made available for the last ten years or so. The plant still calls for further improvements. The processes are only of batch type. For economic running, especially when the system is to be evacuated, continuous processes have to be evolved. The heat transfer of many of the materials is very slow. Limitation of the maximum reaction temperature to about 1200°C. also puts a stop to certain theoretical developments.

Before vacuum processes find wider applications it is necessary that plant materials that resist the attack of the metals and inorganic compounds be made available. Researches on the refractories that would resist the attack of chlorides, fluorides, oxides and sulphides in vacuum are also desirable.

The future of the vacuum technique in metallurgy is undoubtedly large, but will call for great efforts by the metallurgists and technicians in developing the plant materials and equipment.

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Discussions

MR. S. K. MUKHERJEE (Institute of Nuclear Physics)

With reference to the point raised by the authors regarding the availability of diffusion pump, what would be the normal size of a pump to be used with normal-sized system when the system is a kinetic one ? A 14 in. diffusion pump will handle 4000 l/s at 10^{-5} mm. of Hg. Considering that the order of vacuum required is not very high, an ordinary booster type pump with enormous pumping speed will be sufficient. This can be done here in this country. Actually several such pumps have been made in our laboratory.

Authors' Reply

With regard to the points raised by Mr. Mukherjee the normal size is a relative term and would depend on the particular process under operation. It may, however, be pointed out that in the initial stages when vacuum technique was being developed for the production of magnesium, large diffusion pumps were not available that combined high pumping speed in the range 1-500 microns with the ability to operate against high forepressure. Later on, however, both oil and mercury diffusion pumps were developed that were capable of handling extremely large gas volumes at pressures below 1 mm. Hg.

In the systems where there is a continuous evolution of volatiles and the operation is not done under very high vacuum, the booster pumps, as mentioned by Mr. Mukherjee, may serve the purpose.

DR. A. B. CHATTERJEA (National Metallurgical Laboratory)

The authors have referred to the production of magnesium by thermal reduction with ferro-silicon under reduced pressure, as developed by Pidgeon. The reaction is highly endothermic and a consideration of the free energy data would show that the reduction is possible because of two factors: firstly, with the removal of magnesium from the system,

its activity is kept at a low value and its partial pressure is always lower than its reaction pressure, and, secondly, the activity of the silica formed as a reaction product is lowered by its combination with CaO from dolomite. Both these prevent the reverse reaction of the reduction of SiO_2 by Mg.

However, the view expressed by the authors that thermal production of magnesium by the reduction of dolomite by free-silicon has ceased after the last war is not altogether correct. Due to shortage of electric power and other factors, it has been mentioned* that the Manteca (California) plant has

*1. G. L. EVANS, " Non-ferrous Metals — Extraction and Refining ", *Reports on the Progress of Applied Chemistry*, **36** (1951), 283.

2. E. SCHRIER, "Silico-thermic Magnesium Comes Back ", *Chem. Eng.* **59**(4), (1952), 149.

undertaken production of 10,000 tons of magnesium per year and the Mead (Washington) plant is approaching capacity production of 2000 tons/year by the silico-thermal reduction of dolomite.

Authors' Reply

With regard to the points communicated by Dr. Chatterjea the authors have already pointed out that the reaction goes to completion due to the activity of reactants and reaction products and also due to the removal of one of the reduction products.

As regards the shut-down of the plants producing magnesium by Pidgeon's process, the authors have not said that no more magnesium was being produced by this method.