

General Principles and Processes of Isolation of Elements

A few elements like carbon, sulphur, gold and noble gases, occur in free state while others in combined forms in the earth's crust. The extraction and isolation of an element from its combined form involves various principles of chemistry. A particular element may occur in a variety of compounds. The process of metallurgy and isolation should be such that it is chemically feasible and commercially viable. Still, some general principles are common to all the extraction processes of metals. For obtaining a particular metal, first we look for minerals which are naturally occurring chemical substances in the earth's crust obtainable by mining. Out of many minerals in which a metal may be found, only a few are viable to be used as sources of that metal. Such minerals are known as ores. Rarely, an ore contains only a desired substance. It is usually contaminated with earthly or undesired materials known as gangue. The extraction and isolation of metals from ores involve the following major steps:

- Concentration of the ore,
- Isolation of the metal from its concentrated ore, and
- Purification of the metal.

The entire scientific and technological process used for isolation of the metal from its ores is known as **metallurgy**.

Occurrence of Metals: Elements vary in abundance. Among metals, aluminium is the most abundant. It is the third most abundant element in earth's crust (8.3% approx. by weight). It is a major component of many igneous minerals including mica and clays. Many gemstones are impure forms of Al₂O₃ and the impurities range from Cr (in 'ruby') to Co (in 'sapphire'). Iron is the second most abundant metal in the earth's crust. It forms a variety of compounds and their various uses make it a very important element. It is one of the essential elements in biological systems as well. The principal ores of aluminium, iron, copper and zinc have been given below:

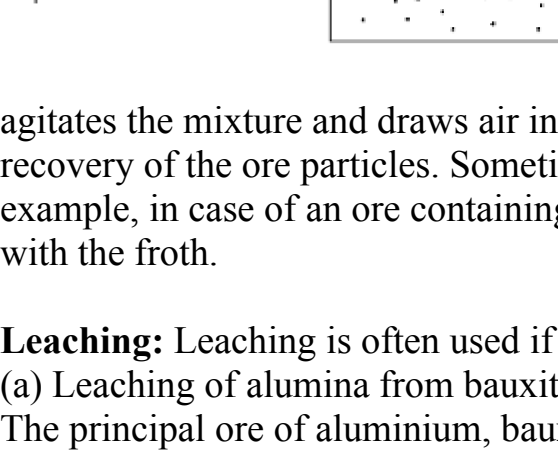
Metal	Ores	Composition
Aluminium	Bauxite	Al ₂ O ₃ (OH) _{3-2x} , (where 0 < x < 1)
	Kaolinite (a form of clay)	[Al ₂ (OH) ₄ Si ₂ O ₅]
Iron	Haematite	Fe ₂ O ₃
	Magnetite	Fe ₃ O ₄
	Siderite	FeCO ₃
	Iron pyrites	FeS ₂
Copper	Copper pyrites	CuFeS ₂
	Malachite	CuCO ₃ ·Cu(OH) ₂
	Cuprite	Cu ₂ O
	Copper glance	Cu ₂ S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	ZnCO ₃
	Zincite	ZnO

For the purpose of extraction, bauxite is chosen for aluminium. For iron, usually the oxide ores which are abundant and do not produce polluting gases (like SO₂ that is produced in case iron pyrites) are taken. For copper and zinc, any of the listed ores may be used depending upon availability and other relevant factors. Before proceeding for concentration, ores are graded and crushed to reasonable size.

Concentration of Ores: Removal of the unwanted materials (e.g., sand, clays, etc.) from the ore is known as concentration, dressing or benefaction. It involves several steps and selection of these steps depends upon the differences in physical properties of the compound of the metal present and that of the gangue. The type of the metal, the available facilities and the environmental factors are also taken into consideration. Some of the important procedures are described below.

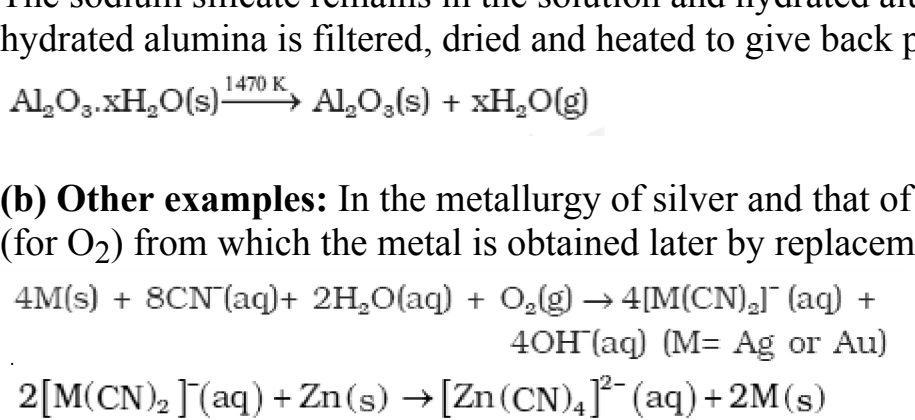
Hydraulic Washing: This is based on the differences in gravities of the ore and the gangue particles. It is therefore a type of gravity separation. In one such process, an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind.

Magnetic Separation: This is based on differences in magnetic properties of the ore components.



If either the ore or the gangue (one of these two) is capable of being attracted by a magnetic field, then such separations are carried out (e.g., in case of iron ores). The ground ore is carried on a conveyer belt which passes over a magnetic roller.

Froth Flotation Method: This method has been in use for removing gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. To it, collectors and froth stabilisers are added. Collectors (e.g., pine oils, fatty acids, xanthates, etc.) enhance non-wettability of the mineral particles and froth stabilisers (e.g., cresols, aniline) stabilise the froth.

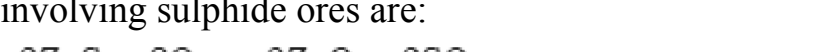


The mineral particles become wet by oils while the gangue particles by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles. Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using 'depressants'. For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

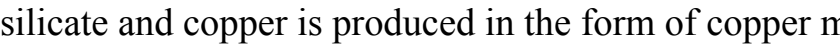
Leaching: Leaching is often used if the ore is soluble in some suitable solvent. The following examples illustrate the procedure:

(a) Leaching of alumina from bauxite:

The principal ore of aluminium, bauxite, usually contains SiO₂, iron oxides and titanium oxide (TiO₂) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473 – 523 K and 35 – 36 bar pressure. This way, Al₂O₃ is leached out as sodium aluminate (and SiO₂ too as sodium silicate) leaving the impurities behind:



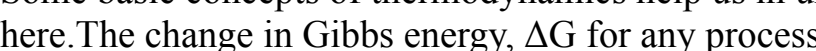
The aluminate in solution is neutralised by passing CO₂ gas and hydrated Al₂O₃ is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated Al₂O₃ which induces the precipitation:



The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al₂O₃:



(b) **Other examples:** In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (or O₂) from which the metal is obtained later by replacement:



Extraction of Crude Metal from Concentrated Ore:

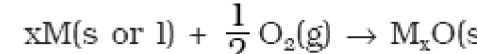
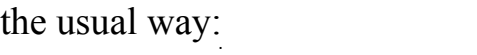
The concentrated ore must be converted into a form which is suitable for reduction. Usually the sulphide ore is converted to oxide before reduction. Oxides are easier to reduce (for the reason see box). Thus isolation of metals from concentrated ore involves two major steps viz.,

- (a) conversion to oxide, and
- (b) reduction of the oxide to metal.

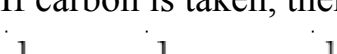
(i) **Calcination:** Calcination involves heating when the volatile matter escapes leaving behind the metal oxide:



(ii) **Roasting:** In roasting, the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal. Some of the reactions involving sulphide ores are:

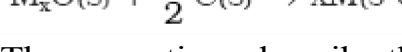


The sulphide ores of copper are heated in reverberatory furnace. If the ore contains iron, it is mixed with silica before heating. Iron oxide 'slags' of iron silicate and copper is produced in the form of copper matte which contains Cu₂S and FeS.



The SO₂ produced is utilised for manufacturing H₂SO₄.

(b) **Reduction of oxide to the metal:** Reduction of the metal oxide usually involves heating it with some other substance acting as a reducing agent (C or CO or even another metal). The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.



Some metal oxides get reduced easily while others are very difficult to be reduced (reduction means electron gain or electronation). In any case, heating is required. To understand the variation in the temperature requirement for thermal reductions (pyrometallurgy) and to predict which element will suit as the reducing agent for a given metal oxide (M_xO_y), Gibbs energy interpretations are made.

Thermodynamic principles of Metallurgy

Some basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations. Gibbs energy is the most significant term here. The change in Gibbs energy, ΔG for any process at any specified temperature, is described by the equation:

$$\Delta G = \Delta H - T\Delta S$$

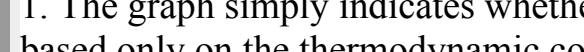
where, ΔH is the enthalpy change and ΔS is the entropy change for the process. For any reaction, this change could also be explained through the equation: ΔG° = – RTlnK

where, K is the equilibrium constant of the 'reactant – product' system at the temperature, T. A negative ΔG implies a +ve K in equation 6.15. And this can happen only when reaction proceeds towards products. From these facts we can make the following conclusions:

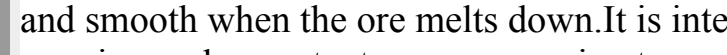
1. When the value of ΔG is negative, only then the reaction will proceed. If ΔS is positive, on increasing the temperature (T), the value of TΔS would increase (ΔH < TΔS) and then ΔG will become –ve.
2. If reactants and products of two reactions are put together in a system and the net ΔG of the two possible reactions is –ve, the overall reaction will occur. So the process of interpretation involves coupling of the two reactions, getting the sum of their ΔG and looking for its magnitude and sign. Such coupling is easily understood through Gibbs energy (ΔG°) vs T plots for formation of the oxides.

The reducing agent forms its oxide when the metal oxide is reduced. The role of reducing agent is to provide ΔG° negative and large enough to make the sum of ΔG° of the two reactions (oxidation of the reducing agent and reduction of the metal oxide) negative.

As we know, during reduction, the oxide of a metal decomposes:



The reducing agent takes away the oxygen. Equation 6.16 can be visualised as reverse of the oxidation of the metal. And then, the ΔfGV value is written in the usual way:



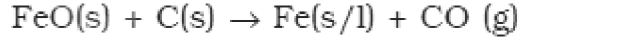
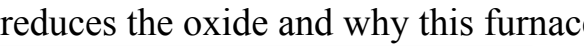
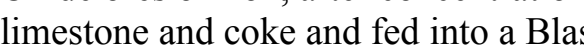
If reduction is being carried out through the above equation, the oxidation of the reducing agent (e.g., C or CO) will be there:



If carbon is taken, there may also be complete oxidation of the element to CO₂:



On subtracting the reduction equation from one of the three oxidation equations, we get:



These reactions describe the actual reduction of the metal oxide, M_xO that we want to accomplish. The Δ_rG° values for these reactions in general, can be obtained by similar subtraction of the corresponding Δ_rG° values.

As we have seen, heating (i.e., increasing T) favours a negative value of Δ_rG°. Therefore, the temperature is chosen such that the sum of Δ_rG° in the two combined redox process is negative. In Δ_rG° vs T plots, this is indicated by the point of intersection of the two curves (curve for M_xO and that for the oxidation of the reducing substance). After that point, the Δ_rG° value becomes more negative for the combined process including the reduction by M_xO. The difference in the two Δ_rG° values after that point determines whether reductions of the oxide of the upper line is feasible by the element represented by the lower line. If the difference is large, the reduction is easier.

Ellingham Diagram:

The graphical representation of Gibbs energy was first used by H.J.T.Ellingham. This provides a sound basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham Diagram. Such diagrams help us in predicting the feasibility of thermal reduction of an ore. The criterion of feasibility is that at a given temperature, Gibbs energy of the reaction must be negative.

(a) Ellingham diagram normally consists of plots of Δ_rG° vs T for formation of oxides of elements i.e., for the reaction,



In this reaction, the gaseous amount (hence molecular randomness) is decreasing from left to right due to the consumption of gases leading to a –ve value of ΔS which changes the sign of the second term in equation. Subsequently ΔG shifts towards higher side despite rising T (normally, ΔG decreases i.e., goes to lower side with increasing temperature). The result is +ve slope in the curve for most of the reactions shown above for formation of M_xO(s).

(b) Each plot is a straight line except when some change in phase (s→liq or liq→g) takes place. The temperature at which such change occurs, is indicated by an increase in the slope on +ve side (e.g., in the Zn, ZnO plot, the melting is indicated by an abrupt change in the curve).

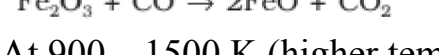
(c) There is a point in a curve below which ΔG is negative (So M_xO is stable). Above this point, M_xO will decompose on its own.

(d) In an Ellingham diagram, the plots of Δ_rG° for oxidation (and therefore reduction of the corresponding species) of common metals and some reducing agents are given. The values of Δ_rG°, etc. (for formation of oxides) at different temperatures are depicted which make the interpretation easy.

(e) Similar diagrams are also constructed for sulphides and halides and it becomes clear why reductions of M_xO is difficult. There, the Δ_rG° of M_xO is not compensated.

Limitations of Ellingham Diagram

1. The graph simply indicates whether a reaction is possible or not i.e., the tendency of reduction with a reducing agent is indicated. This is so because it is based only on the thermodynamic concepts. It does not say about the kinetics of the reduction process (Cannot answer questions like how fast it could be?).
2. The interpretation of Δ_rG° is based on K (ΔG° = – RT lnK). Thus it is presumed that the reactants and products are in equilibrium:

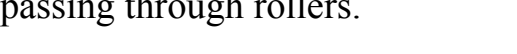


This is not always true because the reactant/product may be solid. [However it explains how the reactions are sluggish when every species is in solid state and smooth when the ore melts down. It is interesting to note here that ΔH (enthalpy change) and the ΔS (entropy change) values for any chemical reaction remain nearly constant even on varying temperature. So the only dominant variable in equation becomes T. However, ΔS depends much on the physical state of the compound. Since entropy depends on disorder or randomness in the system, it will increase if a compound melts (s→l) or vapourises (l→g) since molecular randomness increases on changing the phase from solid to liquid or from liquid to gas].

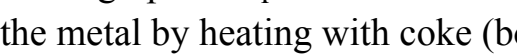
Applications

(a) Extraction of iron from its oxides:

Oxide ores of iron, after concentration through calcination/roasting (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with limestone and coke and fed into a Blast furnace from its top. Here, the oxide is reduced to the metal. Thermodynamics helps us to understand how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process is:



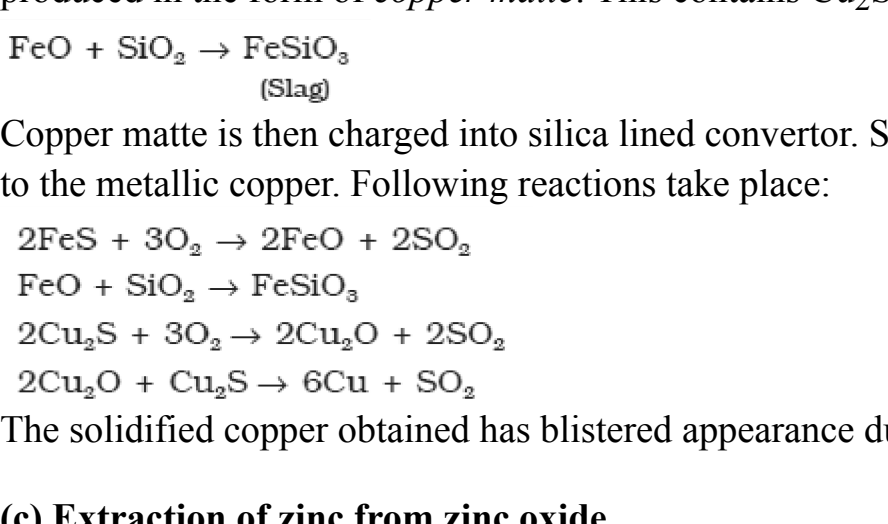
It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO:



When both the reactions take place to yield the overall equation, the net Gibbs energy change becomes:

$$\Delta G^\circ_{C, CO} + \Delta G^\circ_{FeO, Fe} = \Delta_r G^\circ$$

Naturally, the resultant reaction will take place when the right hand side in the above equation is negative. In ΔG° vs T plot representing reaction, the plot goes upward and that representing the change C→CO (C,CO) goes downward. At temperatures above 1073K (approx.), the C,CO line comes below the Fe₂O₃ line [ΔG_r(C,CO) < ΔG_r(Fe₂O₃)]. So in this range, coke will be reducing the FeO and will itself be oxidised to CO. In a similar way the reduction of Fe₃O₄ and Fe₂O₃ at relatively lower temperatures by CO can be explained on the basis of lower lying points of intersection of their curves with the CO, CO₂ curve in the following Figure.

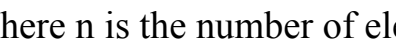
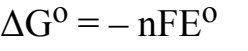


In the Blast furnace, reduction of iron oxides takes place in different temperature ranges. Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto about 2200K in the lower portion itself. The burning of coke therefore supplies most of the heat required in the process. The CO and heat moves to upper part of the furnace. In upper part, the temperature is lower and the iron oxides (Fe₂O₃ and Fe₃O₄) coming from the top are reduced in steps to FeO. Thus, the reduction reactions taking place in the lower temperature range and in the higher temperature range, depend on the points of corresponding intersections in the Δ_rG° vs T plots. These reactions can be summarised as follows:

At 500 – 800 K (lower temperature range in the blast furnace)–



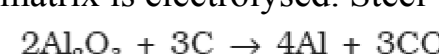
At 900 – 1500 K (higher temperature range in the blast furnace):



Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron. The iron obtained from blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn). This is known as pig iron and cast into variety of shapes. Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Wrought Reductions:

Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide:



Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag. The metal is removed and freed from the slag by passing through rollers.

(b) Extraction of copper from cuprous oxide [copper(I) oxide]:

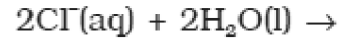
In the graph of Δ_rG° vs T for formation of oxides shown above, the Cu₂O line is almost at the top. So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C, CO₂ are at much lower positions in the graph particularly after 500 – 600K). However most of the ores are sulphide and some may also contain iron. The sulphide ores are roasted/smelted to give oxides:



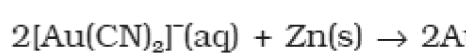
The oxide can then be easily reduced to metallic copper using coke:



In actual process, the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags' of iron silicate and copper is produced in the form of *copper matte*. This contains Cu₂S and FeS.



Copper matte is then charged into silica lined convertor. Some silica is also added and hot air blast is blown to convert the remaining FeS, FeO and Cu₂S/Cu₂O to the metallic copper. Following reactions take place:



The solidified copper has blistered appearance due to the evolution of SO₂ and so it is called **blister copper**.

(c) Extraction of zinc from zinc oxide

The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper. For the purpose of heating, the oxide is made into bricks/tiles with coke and clay.



The metal is distilled off and collected by rapid chilling.

Electrochemical Principles of Metallurgy

We have seen how principles of thermodynamics are applied to pyrometallurgy. Similar principles are effective in the reductions of metal ions in solution or molten state. Here they are reduced by electrolysis or by adding some reducing element. In the reduction of a molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation,

$$\Delta G^\circ = -nFE^\circ$$

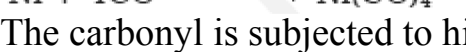
Here n is the number of electrons and E° is the electrode potential of the redox couple formed in the system. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two E° values corresponds to a positive E° and consequently negative ΔG° in the above equation, then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g.,



In simple electrolysis, the Mⁿ⁺ ions are discharged at negative electrodes (cathodes) and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added for making the molten mass more conducting.

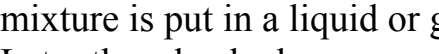
Aluminium

In the metallurgy of aluminium, purified Al₂O₃ is mixed with Na₃AlF₆ or CaF₂ which lowers the melting point of the mix and brings conductivity. The fused matrix is electrolysed. Steel vessel with lining of carbon acts as cathode and graphite anode is used. The overall reaction may be written as:



This process of electrolysis is widely known as Hall-Heroult process.

Thus electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO₂. This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are:



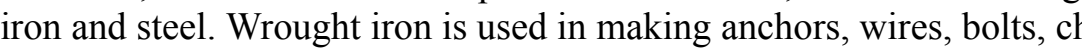
Copper from Low Grade Ores and Scraps

Copper is extracted by hydrometallurgy from low grade ores. It is leached out using acid or bacteria. The solution containing Cu²⁺ is treated with scrap iron or H₂



Oxidation Reduction

Besides reductions, some extractions are based on oxidation particularly for non-metals. A very common example of extraction based on oxidation is the extraction of chlorine from brine (chlorine is abundant in sea water as common salt).



The ΔG° for this reaction is + 422 kJ. When it is converted to E° (using ΔG° = – nFE°), we get E° = – 2.2 V. Naturally, it will require an external e.m.f. that is greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions. Thus, Cl₂ is obtained by electrolysis giving out H₂ and aqueous NaOH as byproducts. Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH.

As studied earlier, extraction of gold and silver involves leaching the metal with CN[–]. This is also an oxidation reaction (Ag → Ag⁺ or Au → Au⁺). The metal is later recovered by displacement method.

In this reaction zinc acts as a reducing agent.

Refining: A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below.

- (a) Distillation
- (b) Liquefaction
- (c) Electrolysis