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Modern Chemistry
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Incorporating Metropolitan College
Founded 1894

Lesson 33

SET WORK

SUBJECT: The principles of metal extraction.

READING: Parts of Chapter 30 of Mathews.

N O T E S

PRINCIPLES OF METAL EXTRACTION

INTRODUCTION

The most important factor in the method chosen to obtain a metal from an ore is the position which the metal holds in the reactivity series (electro-chemical series). Some of the more common elements are placed in the reactivity series as follows:

Potassium

Calcium

Sodium

Magnesium

Aluminium

t t Carbon H

Zinc

Iron

Tin

Lead

Copper

Silver

The general principle of the reactivity series is that a compound of a metal low in the reactivity series will react with a metal high in the reactivity series, undergoing a displacement reaction. Simple reactions which have been met before and demonstrate this are;

$\text{CuSO}_4 + \text{Fe} \rightarrow \text{FeSO}_4 + \text{Cu}$

(3(1) (3(1)

heat

$3\text{PbO}_2 + 4\text{Al} \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Pb}$

What is of the greatest importance however, is the position of carbon in the reactivity series. Carbon is very cheap and can react with oxide ores from the metals below it, in effect being a reducing agent. From this we can make some general rules about the principles of metal extraction:

1. Metals above carbon in the reactivity series cannot be removed from their ores by using carbon. They are generally removed by electrolysis of the molten ore.

2 . Metals below carbon in the reactivity series may be removed from their ores (usually oxides), using carbon.

3 . A few metals below carbon in the reactivity series are removed from their ores using a more expensive reducing agent than carbon, but this is due to the lower activation energy needed to initiate the reaction. The expensive reducing agent and lower energy cost outweighs the cheap reducing agent and high energy cost.

4. One or two metals have very specialised manufacturing processes which considerably adds to their cost.

THE EXTRACTION OF SOME METALS

SODIUM

Sodium must be isolated from the sodium chloride in the sea. Salt from salt beds, dried by the sun, has some calcium chloride added to it to lower its melting point from about 800°C to 600°C. It is then electrolysed in a Downs Cell, where chlorine is a valuable by-product. Molten sodium metal forms at an iron cathode and chlorine is released at a graphite anode. The two products, which would otherwise react, are kept apart using a steel diaphragm.

The equations for the reaction are:

At the

At the cathode: $2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{Na}$

At the anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

ALUMINIUM

Aluminium is also above carbon in the reactivity series and so cannot be removed from any ore using carbon. This means that electrolysis of a molten ore is the only feasible way to obtain aluminium. This process is further complicated by the fact that aluminium oxide ore, bauxite, is a non-electrolyte with a high melting point. The problem is solved by adding cryolite, sodium aluminium fluoride, to the bauxite; this both converts the resulting melt into an electrolyte and also lowers the overall melting point.

The resulting mixture of bauxite and cryolite is electrolysed molten in a cell using graphite anodes and cathodes. The quantity of electricity used by this process is high for the weight of aluminium deposited (remember from a previous Lesson that it takes 3 Faradays of electricity to deposit 1 mole of aluminium - just 27g). Aluminium plants tend to be situated near to hydro-electric power plants, therefore, and the metal is costly due to the power consumed.

The equations for the reaction are:

At the

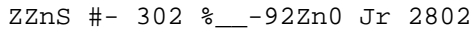
At the cathode: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

At the anode: $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$

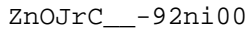
ZINC

Zinc is below carbon in the reactivity series, so reduction with carbon ought to, and does, prove the best way to isolate zinc metal.

Zinc occurs in nature as zinc blende, a form of zinc sulphide. This is first roasted in air to form zinc oxide:



The oxide is then heated in a furnace with powdered coke to bring about the reduction to the metal;

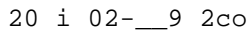


Zinc has a fairly low boiling point, and so is collected by condensing its vapour in the above reaction, yielding a very pure product.

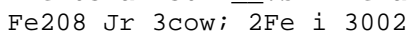
IRON

Iron can also be, and is, separated from its ores by carbon reduction, The process, that of the blast furnace, is more complicated than the zinc extraction process.

Iron ore (haematite) is broken into lumps and added to the blast furnace along with coke and limestone, and the mixture is heated with a blast of hot air. A series of reactions then take place within the body of the furnace. Some of the coke is oxidized to carbon monoxide by the blast of hot air:

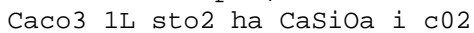


Either coke or carbon monoxide can then act as reducing agents to reduce the haematite to iron;



The first reaction, that with iron oxide and carbon takes place in the hot lower regions of the furnace at temperatures above 700°C, the reaction with carbon monoxide takes place higher where the temperatures are much lower.

The limestone is added to remove impurities from the furnace. With sand for example, the following reaction takes place:



The calcium silicate formed drains away as a molten slag, effectively removing impurities from the reactants in a very cost-effective way.

COPPER

Copper exists as copper pyrites, a mixed ore, CuFeS_2 . This ore is crushed, concentrated, and then roasted in a limited supply of air:

$2\text{CuFeS}_2 \rightarrow \text{Jr } 402\text{-a}_-3\text{Cu}_2\text{S} + 2\text{FeO} + \text{Jr } \text{BSO}_2$

Silica is then added to remove the iron(II) oxide as a slag, leaving copper(I) sulphide. The sulphide is then heated in a controlled supply of air to turn it into the impure metal;

$\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu} + \text{SO}_2$

The metal is then refined electrolytically to give the pure metal. It is used as the anode in a cell which uses copper sulphate as the electrolyte; the impure anode dissolves and pure copper builds up on the cathode.

As the anode dissolves, a sludge known as anode slime remains behind.

This contains trace quantities of gold, platinum and other rare metals which are recoverable and so help the economics of the process.

CHROMIUM

Chromium is obtained in a rather complicated process, due to both the fact that it occurs as a mixed ore, and to reduction with carbon being non-economic.

Chromite ore, FeCr_2O_4 is strongly heated with sodium carbonate in the presence of air to form sodium chromate;

$4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 4\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$

Sulphuric acid is then added; this yields sodium sulphate which first crystallises out, followed by sodium dichromate:

$2\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} + \text{H}_2\text{SO}_4$

Reaction with carbon then follows to convert the sodium dichromate to chromium(III) oxide:

$\text{Na}_2\text{Cr}_2\text{O}_7 + 4\text{C} \rightarrow 2\text{Cr}_2\text{O}_3 + 2\text{Na}_2\text{CO}_3 + 4\text{CO}$

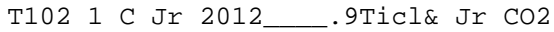
The above reaction requires strong heat; to reduce chromium(III) oxide to chromium requires even more energy, so much so that it is cheaper to use aluminium metal and a lower temperature as the reducing agent:

$\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3$

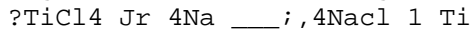
TITANIUM

Titanium, an element quite common in the earth's crust, is made expensive by the cost of the manufacturing process. It occurs as rutile, TiO_2 , an ore which is very resistant to reduction, thus removing the possibility of cheap reduction with carbon.

Rutile is heated with carbon in a stream of chlorine, not for reduction but to turn it into titanium chloride a liquid at room temperature:



The liquid is purified by distillation and then reduced with metallic sodium or magnesium which adds significantly to the cost;



TEST 33

1. The following fictitious metals are placed in a reactivity series with carbon:

Blackium

Blueium

Greenium

Carbon

Pinkium

Whiteium

: Radium

(Brownium

(3) Which metals will pinkium oxide react with?

(b) Which metals will whiteium oxide not react with?

(0) Name two metals in the list which are likely to be removed and isolated by electrolysis of a molten halide.

(d) Which two metals are most likely to be isolated by heating with coke?

(9) Which metal in the list is most likely to occur in nature as a free metal, not as an ore?

(f) Which of the metals is most likely to not occur in sea water but still be electrolysed out of a melt?

(g) Which metal is most likely to be obtained using a Downs Cell?

2. Carbon lies between aluminium and iron in the reactivity series. Explain how this affects the way in which these two metals are obtained from their oxide ores.

3 . Discuss the way in which copper and titanium are manufactured.
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Specimen Answers to Test 32

Iron is obtained from iron ore in a blast-furnace. As well as the ore, the chemical reaction needs heat, coke and limestone. Ironworks are sited on iron ore deposits or coalfields to cut down transportation costs of one of the raw materials involved.

The blast-furnace reaction is cheap to produce, Iron ore, limestone and coke are all comparatively cheap materials. The heat needed is the only expensive commodity, so this is re-cycled wherever possible.

Aluminium ores are not as plentiful as they would at first seem. Although much more abundant than iron in percentage terms, much aluminium occurs in aluminosilicate clays from which no satisfactory method of removing aluminium has been found.

To make aluminium metal, the ore bauxite needs to be electrolysed in a molten state, which uses up vast quantities of electricity. Apart from the melting process, the electrolysis is very demanding on power also. The aluminium ion is charged $3+$, so 3 Faradays of electricity are needed to deposit one mole of aluminium, just 27g.

Transportation costs are not therefore a significant factor. The apparent contradiction between the availability of aluminium and iron and their abundances is due to the nature of some of the aluminium ores and the consuming nature of aluminium's production process.

Limestone finds greatest use in the production of cement and concrete. To make cement it is heated with sand and a silicate such as clay; on adding water a complex chemical reaction takes place and the mixture hardens. Concrete is formed by mixing cement with small stones and sand, on adding water the mixture again hardens, forming a more durable product than cement. Limestone is also used in the blast-furnace production of iron. It reacts with silicate impurities in iron ore which it removes as slag. It also finds use in gardening and agriculture, for which it is turned into quick-lime which is added to acid soils to neutralise them.

Rock salt is used in large quantities in cold climates to melt ice on roads. Any electrolyte added to water lowers its melting point, and rock salt is the cheapest material available to do this. It has the disadvantage, however, of being a very corrosive material, attacking soft steel and iron and causing damage to motor vehicles.

Molten rock salt can be used as a source of sodium, but it is more economic to use salt obtained from sea water. Rock salt tends to need more purification, and also needs to be mined or quarried. In hot climates thermal energy can be used to evaporate sea water to dryness,

yielding easily accessible, cleaner salt.

Oxygen and nitrogen are obtained from the air by fractional distillation of liquid air. Air has its water vapour, carbon dioxide and any dust removed, and is then compressed to about 200 atmospheres and allowed to cool. On releasing the pressure, the temperature drops considerably and the air liquefies. As the liquid warms, nitrogen boils off at -196°C , followed by oxygen at -183°C .

Chlorine is obtained as a by-product in the manufacture of metallic sodium. In the Downs Cell process molten salt is electrolysed, which is bound to yield chlorine as the product at the anode.

Methane is obtained from natural gas. It is usually contaminated with traces of hydrogen and carbon monoxide, but, since it is usually used as a fuel and the contaminants themselves are combustible, they need not be removed.

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