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ALTERNATIVE REDUCTANTS

Introduction

1)Shredder residue materials

Shredder residue materials are produced after the removal of ferrous and non-ferrous fractions from end-of-life electronic equipment. Despite the high plastic content and metal value in the ash, high percentages of these materials are currently sent to landfills.

The shredding of automobiles and major household appliances is a process where a hammermill acts as a giant tree chipper by grinding the materials fed into it to fist-size pieces. The shredding of automobiles results in a mixture of ferrous metal, non-ferrous metal (e.g. alloys of copper and aluminium) and shredder waste, called automotive shredder residue or automobile shredder residue (ASR). ASR consists of glass, fiber, rubber, automobile liquids, plastics and dirt. ASR is sometimes differentiated into shredder light fraction and dust. Sometimes these residual materials are called "car-fluff".



ASR often contains hazardous substances such as lead, cadmium, and PCB. Therefore, some countries have classified ASR as hazardous waste and have established legislative controls.

RECYCLING

It is estimated that every year in EU nations nearly 3 million tonnes of automotive shredder residue (ASR) are generated. While half of the waste which contains rubber, textiles and plastics can be transferred into alternative fuels or recycled, the remaining portion is primarily land-filled. The European Draft directive 2000/53/CE states that by the year 2015, only 5% of the vehicle's weight can be disposed of at landfill sites.

Recycling techniques

ASR waste contains 30% organic matter and inorganic compounds such as lead, zinc, quartz, calcite, magnetite, anhydrite and hematite. Some of the methods to recycle ASR are:

- *Using as a retarder for ordinary Portland cement by transformation into aggregates after thermal treatment followed by chemical treatment.*
- *Conversion of automobile plastic residue into synthetic crude oil. This technology is patented by Agilyx.*
- *Recycling thermoplastic materials from residue plastic which can be used in construction and agriculture sector.*
- *Use of thermo-chemical processes, such as pyrolysis or gasification.*

2)Charcoal from agricultural residue

Charcoal is a lightweight black carbon residue produced by strongly heating wood (or other animal and plant materials) in minimal oxygen to remove all water and volatile constituents. In the traditional version of this pyrolysis process, called charcoal burning, the heat is supplied by burning part of the starting material itself, with a limited supply of oxygen. The material can also be heated in a closed retort.

This process happens inadvertently while burning wood, as in a fireplace or wood stove. The visible flame in these is due to combustion of the volatile gases exuded as the wood turns into charcoal. The soot and smoke commonly given off by wood fires result from incomplete combustion of those volatiles. Charcoal burns at a higher temperature than wood, with hardly a visible flame, and releases almost nothing except heat.



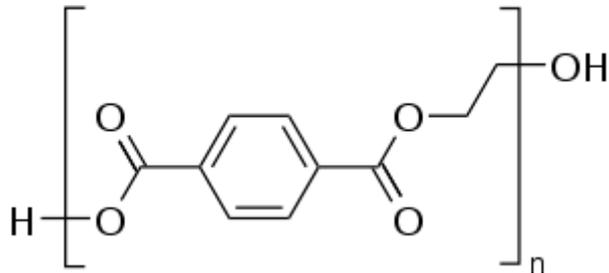
3)Waste polyethylene terephthalate

Polyethylene terephthalate (sometimes written poly(ethylene terephthalate)), commonly abbreviated PET, PETE, or the obsolete PETP or PET-P, is the most common thermoplastic polymer resin of the polyester family and is used in fibres for clothing, containers for

liquids and foods, and thermoforming for manufacturing, and in combination with glass fibre for engineering [resins](#).

It may also be referred to by the brand names Terylene in the UK, Lavan in Russia and the former Soviet Union, and Dacron in the US.

Bio-PET is the bio-based counterpart of PET.



The majority of the world's PET production is for synthetic fibres (in excess of 60%), with bottle production accounting for about 30% of global demand. In the context of textile applications, PET is referred to by its common name, polyester, whereas the acronym PET is generally used in relation to packaging. Polyester makes up about 18% of world polymer production and is the fourth-most-produced polymer after polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC).

PET consists of polymerized units of the monomer ethylene terephthalate, with repeating (C₁₀H₈O₄) units. PET is commonly recycled, and has the number "1" as its resin identification code (RIC).

Depending on its processing and thermal history, polyethylene terephthalate may exist both as an amorphous (transparent) and as a semi-crystalline polymer. The semicrystalline material might appear transparent (particle size less than 500 nm) or opaque and white (particle size up to a few micrometers) depending on its crystal structure and particle size.

The monomer bis(2-hydroxyethyl) terephthalate can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct (this is also known as a condensation reaction), or by transesterification reaction between ethylene glycol and dimethyl terephthalate (DMT) with methanol as a byproduct. Polymerization is through a polycondensation reaction of the monomers (done immediately after esterification/transesterification) with water as the by product.

[4\)Hydrogen Plasma](#)

HP is obtained by hydrogen gas (H₂), which is available in large quantities in water and is collected from splitting of water .

They can be produced by application of DC or AC voltage, or by a radio frequency or microwave electromagnetic field. HP consists of ro-vibrationally excited molecular (H₂*), atomic (H), and ionic hydrogen (H⁺), which can reduce the iron oxides, even at low temperatures.

The process has extensive potential with respect to technoeconomic feasibility. Due to the elimination of multiple processes like palletisation, coke making, sintering, etc., the new process requires less energy. Due to the elimination of multiple processes like palletisation, coke making, sintering, etc., the new process requires less energy. The process has extensive potential with respect to the techno-economic.

By this method iron can be produced at a cost 20% less, compared to the blast furnace iron making process. It has another reason of this reduction of cost, energy carried by these hydrogen species are released at reduction interface causing local heating favouring the reduction. In the recent studies, by using low-temperature microwave hydrogen plasma, production of metals like Fe from Fe₂O₃, Cu from CuO, Co from Co₃O₄, and alloys like CuNi alloy, FeCo alloy, etc., from the reduction of metal oxide mixtures, have been reported.



Hydrogen as reductant

Introduction

Hydrogen shows a lot of different advantages as reducing agent for metallurgical purposes. Fast reaction rates as well as the formation of easy condensable water damp are the most important benefits .

In principle, hydrogen can be applied as a reducing agent for the production of many metals. It has found commercial application for the synthesis of platinum group metals, some rare metals such as germanium and rhenium, and for the production of special grades of metals (e.g., fine nickel and cobalt powders) .However, hydrogen is primarily applied for the synthesis of tungsten and molybdenum, with very pure metal powders resulting from the hydrogen reduction of their oxides.

Metals rarely occur in pure form; only the precious metals mercury and copper are exceptions. The others are bonded to oxygen, sulfur, and, infrequently, halogenides. Therefore, the metals must be separated from these nonmetals by reduction, which can be executed in different ways. Four basic reduction processes are reduction by carbon, carbon monoxide, or hydrogen; metallothermic reduction; aqueous electrolysis; and molten salt electrolysis.

Of these four possibilities, hydrogen is not used for the production of major metals such as iron, copper, and aluminum. Nevertheless, it is applied for the synthesis of two refractory metals, tungsten and molybdenum, because every pure metal powders are achieved by hydrogen reduction of their oxides. It is also used for the fabrication of some other metals, such as platinum and rhenium, and for the manufacture of special metal grades, mainly fine metal powders.

The extraction of very pure metals, mostly in the form of powder by a gas-solid reaction is a great advantage of hydrogen as a reductant and so no refining of the obtained metal is necessary. This is enabled by using pure compounds as raw materials and pure hydrogen for the reduction; only water vapor is liberated as a by-product.

- **Various Reactions of hydrogen as Reduction agent**

1. **Iron Reduction:**



In general, the reduction of Fe₂O₃, called hematite, does not occur directly to metallic iron, therefore hydrogen is used as reductant to carry forward extraction process of iron metal

2. **Cobalt and germanium reduction:**

- $\text{Co}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Co} + 4\text{H}_2\text{O}$
- $\text{GeO}_2 + 2\text{H}_2 \rightarrow \text{Ge} + 2\text{H}_2\text{O}$

Pure hydrogen gas is passed over oxides of cobalt and germanium which remove the oxygen component and make the metal free from its oxide.

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4. **Molybdenum and tungsten reduction:**

- $2\text{NH}_4[\text{MoO}_4] + 7\text{H}_2 \rightarrow 2\text{Mo} + 8\text{H}_2\text{O} + 2\text{NH}_3$
- $2\text{NH}_3[\text{WO}_4] + 7\text{H}_2 \rightarrow 2\text{W} + 8\text{H}_2\text{O} + 2\text{NH}_3$

Certain metallic oxides can be reduced using molecular hydrogen. Because of inflammable nature of hydrogen, it is used in very few cases. Molybdenum and tungsten are obtained by reducing their oxides by hydrogen at elevated temperatures.

REDUCTION OF TIN

In the conventional smelting of tin, large amount of carbon dioxide together with tin metal is inevitably emitted from the two stage carbothermal reduction.

Oxide form of tin SnO₂ is reduced by hydrogen to obtain pure form of tin. The reduction of SnO₂ by hydrogen is of interest as a means of diminishing carbon dioxide emission in the tin smelting processes. The reduction reaction can be represented by:-

- $\text{SnO}_2 + 2\text{H}_2(\text{g}) = \text{Sn}(\text{s}, \text{l}) + 2\text{H}_2\text{O}(\text{g})$

Table show Collection efficiencies for elements obtained from their oxides by hydrogen reduction

Oxide/metal	Reduction temperature (K)	Time (min)	Melting point (K)	Efficiency (%)
CuO/Cu	970	120	1356	99.8
In ₂ O ₃ /In	970	120	430	99.5
SnO ₂ /Sn	970	120	505	99.8
PbO/Pb	770	60	601	99.9
GeO ₂ /Ge	970	105	1210	99.4
WO ₃ /W	1170	120	3680	99.9
Fe ₂ O ₃ /Fe	970	150	1808	99.8
NiO/Ni	970	60	1726	99.5

**POTENTIAL OF HYDROGEN AS ALTERNATIVE REDUCING AGENT
IN METALLURGICAL PROCESSES**

The high price of hydrogen compared to the alternatively used carbon is the reason why today hydrogen only plays a minor role in metallurgical processes. Some applications can be found in direct reduction processes of iron ore as well as some areas in nonferrous metallurgy like nickel production and the reduction of refractory metal oxides.

One option to allow a better economy could be to prevent the use of hydrogen in its pure form by using hydrogen containing gases like reforming or pyrolysis gases. Especially in the development and optimization of recycling processes the tendency is to avoid high CO₂ emissions for example by the substitution of carbon by hydrogen.

Typical heavy metal containing wastes like dusts from steel industry contain high amounts of recoverable zinc beside iron and lead. Therefore the idea is to recover zinc by reduction and vaporization while simultaneously iron oxides are reduced, forming an iron sponge that could be reused in steel industry.

Laboratory experiments were done in the field of hydrogen reduction of heavy metal containing residues show promising results concerning the **metallurgical feasibility.**

Today recycling of industrial wastes is an important field because of the chance to minimize landfilling, to recover valuable metals and therefore save primary resources and to lower the energy demand. Especially in the metallurgical business these recycling processes are based on carbothermal principles emitting high amounts of CO₂ into the atmosphere. **Rising recycling rates clearly show the need for an alternative reductant like for example hydrogen.**

METALLOTHERMIC REDUCTION

INTRODUCTION

Metallothermic reduction reactions (MRRs) are displacement reactions that use reactive metals to reduce compounds so that metals, alloys, nonmetal elementary substances, and composites are produced, often in a scalable manner for applications, including energy storage, gas adsorption, and catalysis. In recent years, nonmetal materials, mainly silicon and carbon, particularly in their nanostructured forms, obtained using a MRR with magnesium as the reductant starts to attract much attention. However, reactions using other metals as the reductant have not been widely looked at yet. Furthermore, the reaction mechanisms and their controlling factors still remain unclear, and much more endeavors are needed to strengthen this emerging field.

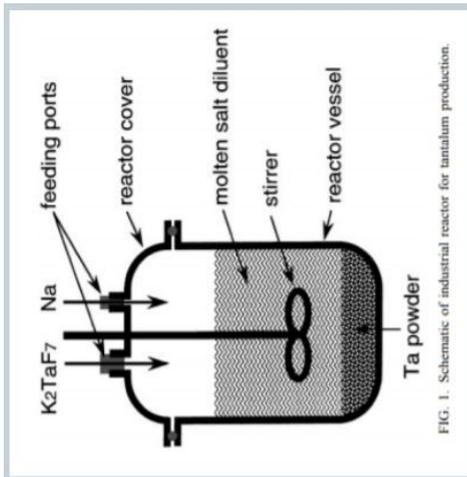
MRR AS AN ELECTRONICALLY MEDIATED REACTION

In a study of the production of tantalum powder by the reaction of K₂TaF₇ with sodium in a molten salt medium at 850 C, it has been shown that there are two dominant kinetic pathways, both involving electron transfer. Furthermore, the overall rate of reaction is limited by electron transport between the reactants. Hence, we have dubbed metallothermic reduction an “electronically mediated reaction” (EMR).

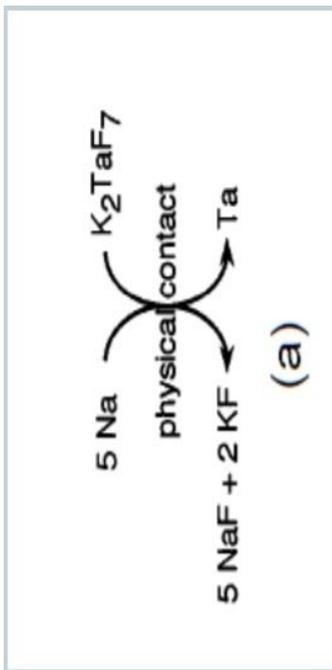
Tantalum is produced by Metallothermic reduction of one of its salts. At approximately 800 C, solid K₂TaF₇ and liquid Na are added to a halide melt where they react to produce solid tantalum in the form of powder.

The central reaction for the process is:

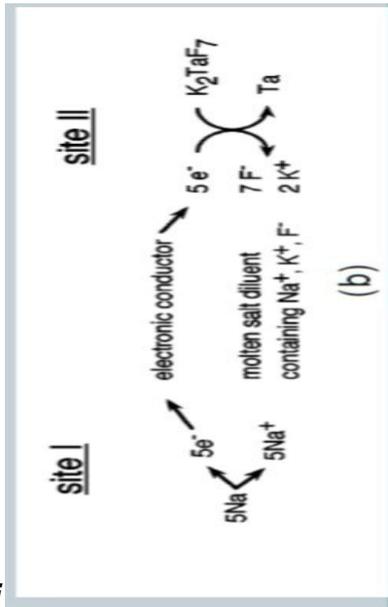




Conventional metallothermic reduction is based on direct physical contact between feed and reductant as shown. Mixing of feed and reductant is achieved by mass transport through the reaction medium. The mechanism includes electron-transfer steps together with the transport of electrons between reactants.

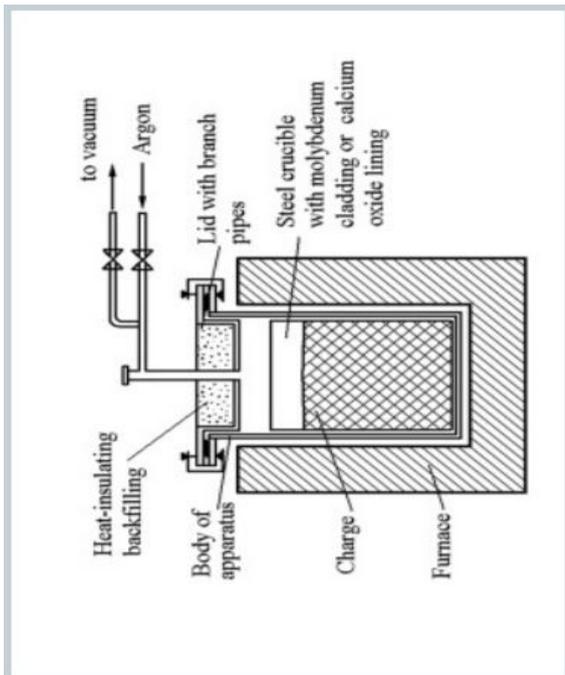


When EMR is operative, the reactor can be viewed as functioning much like a primary battery. The reductant acts as the anode or electron source, the diluent acts as the electrolyte, and the metal product acts as the cathode or electron sink. A metallic object that contains both sodium and K₂TaF₇ functions as the load in such a battery circuit and provides a low-resistance path for the electrons.



Mi

Calcium reduction of thorium-dioxide:



MRRs have been known for more than two centuries. As a manufacturing method, it has been widely employed for the industrial production of metals and alloys. Recently, the syntheses of advanced structures of nonmetals by MRRs have shown their versatile capability, where pioneering examples have been reported for the preparation of nanostructured silicon and nanoporous carbon/graphene. Most recently, MRRs have been demonstrated capable of preparing nanocomposites, e.g., Li₂S@graphene. MRRs can

be reactions between liquid and solid, between vapor and solid, between vapor and liquid, or perhaps between vapor and vapor, where the metal reductants can be either liquid or vapor.

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- *Encyclopedia Britannica*