# Recycling In circular economy 

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## Outline

1. The Technical Cycle and the Biological Cycle
2. The Technical Cycle Related SWM Businesses
3. The Biological Cycle Related SWM Businesses
4. Concluding Remarks

Annex: Recycling in the chemical industry

## 1. The Technical Cycle and The Biological Cycle

- The Biological Cycle and the Technical Cycle shown on the figure are over-simplification of reality.
- Waste is generated at all steps in the life-cycle of materials and products, starting with raw materials extraction, followed by manufacturing, followed by products distribution and retail, and finally product at End-of-Life (EOL).
- In the circular economy, wastes from each step can enter numerous feedback loops, or be utilized for energy recovery, or go to disposal in a landfill.


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## 2. The Technical Cycles WM Related Businesses



## Main References



### 2.1. Introduction

- Material consumption global average is 5 ton/person/year
- Distinction between non-renewable resources (minerals and oil) and renewable resources (e.g biomass). There is an interrelation since the second needs nutrients (e.g P and K) and micronutrients (e.g Selenium)
- Recycling is targeted for non-renewable resources as well as renewable resources. Recycling of renewable resources (such as paper) contributes to more efficient supply of resources ( land, water and energy)


### 2.1. Introduction "cont."

- Recycling rates differ per material recycled. According to the industry itself, the global recycling rate of paper is currently $56 \%$ (ICFPA, 2013 ). Europe is the leader, with a paper recycling rate of $70 \%$.
- Recycling rates for metals vary from very high (gold) to negligible for many specialty metals, such as lithium and tellurium. Recycling rates tend to be higher when the metals are used in large quantities in easily recoverable applications (e.g. lead in batteries, steel in automobiles) or when they have a high value.
- Increasingly however, small quantities of (rare) metals are used in complex products such mobile phones.
- In this context, Porter (2002) distinguishes between economies of scale in recycling (unit costs of recycling go down when the supply of waste material increases) and diseconomies of scope (unit costs of recycling go up when the number of different recyclable materials and applications increases.


### 2.2. Waste Sources and Definitions

1. Production or consumption residues
2. Off-specification products
3. Products whose date for appropriate use has expired
4. Materials spilled, lost or having undergone other mishap, including any materials, equipment, etc., contaminated as a result of the mishap
5. Materials contaminated or soiled as a result of planned actions (e.g. residues from cleaning operations, packing materials, containers, etc.)
6. Unusable parts (e.g. reject batteries, exhausted catalysts, etc.)
7. Substances which no longer perform satisfactorily (e.g. contaminated acids, contaminated solvents, etc.)
8. Residues of industrial processes (e.g. slags, still bottoms, etc.)

## Waste Sources and Definitions, cont'd.

9. Residues of industrial processes (e.g. slags, still bottoms, etc.)
10. Residues from pollution abatement processes (e.g. scrubber sludge, baghouse dusts, spent filters, etc.)
11. Machining/finishing residues (e.g. lathe turnings, mill scales, etc.)
12. Residues from raw materials extraction and processing (e.g. mining residues, oil field slops, etc.)
13. Adulterated materials (e.g. oils contaminated with PCBs, etc.)
14. Any materials, substances or products whose use has been banned by law
15. Products for which the holder has no further use (e.g. agricultural, household, office, commercial, etc.)
16. Contaminated materials, substances or products resulting from remedial action with respect to land any materials, substances or products which are not contained in the above categories.

### 2.3. Secondary Materials Market

- The waste industry depends closely on the secondary materials in its local and foreign markets.
- Some markets are relatively local, for example for compost or for aggregates from C\&D waste. Others may be national or regional, such as for glass and alternative fuels made from MSW
- The secondary materials which are globally traded commodities include ferrous and non-ferrous metals, paper and board ('recovered paper' or 'recovered cellulose fiber'), plastics and textiles. The use of recycled materials competes with and displaces the use of primary materials and helps reduce the extraction of virgin material resources and reduce greenhouse gas emissions.
- In 2010, 700 to 800 million tons of "waste" were recycled as "secondary commodities", derived from MSW as well as other waste streams.
- In terms of both tonnage and value, recycling markets are dominated by ferrous scrap (steel). In tonnage terms this is followed by paper and board, whereas in terms of value non-ferrous metals rank second, with aluminum and copper dominating this market.
- Only a relatively small proportion of the total 700 to 800 million tons (likely less than $25 \%$ ) is traded across national boundaries.
- Asia makes up the most dynamic and arguably the most important global recycling market


## Total turnover of recycling of seven key recyclables in the EU, 2004 and 2006-2009



EEA Report, Earnings, jobs and innovation: the role of recycling in a green economy, 2011

### 2.3.1 Ferrous Metals

- Every ton of ferrous metal scrap that goes back into production reduces the use of iron ore by $1,400 \mathrm{~kg}$, of coal by 740 kg , and of limestone by 120 kg .
- The figure shows a steady increase in scrap use from 2001-2014, By 2011-2014, total steel scrap use was approaching 600 million tpa, approximately $40 \%$ of total steel production.
- Scrap can be grouped into the three sources of (i) post-consumer (old) scrap; (ii) new scrap (e.g. production off-cuts) purchased by steel mills from industrial users; and (iii) own arising, directly recycled within the steel mills (rejects from melting, casting and rolling)



### 2.3.2 Non-Ferrous Metals

| COMMODITY | GLOBAL DEMAND FOR METAL* |  |  | GLOBAL SCRAP CONSUMPTION |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2000 (Million tonnes) | 2011 <br> (Million tonnes) | $\begin{aligned} & \text { Percentage } \\ & \text { growth } \\ & 2000-2011^{*} \end{aligned}$ | 2000 (Million tonnes) | (Million tonnes) | $\begin{aligned} & \text { Percentage } \\ & \text { growth } \\ & 2000-2011 \end{aligned}$ |
| Aluminium | 25 | 45 | 82\% | 11 | 18 | 68\% |
| Copper | 15 | 19 | 30\% | 7.0 | 10 | 45\% |
| Lead | 9 | 12 | 30\% | 3.7 | 5.8 | 57\% |
| Zinc | 7 | 10 | 40\% | 0.8 | 1.1 | 34\% |
| Nickel | 1 | 1.1 | 10\% | 0.6 | 0.9 | 42\% |
| Steel | 1144 <br> (2005 data) | 1607 | (40\%) | 401 | 573 | 43\% |

## Life Cycle of Metals and End-Of-Life Products

Flows related to a simplified life cycle of metals and the recycling of production scrap and end-oflife products. Boxes indicate the main processes (life stages): Prod, production; Fab, fabrication; Mfg, manufacturing; WM\&R, waste management and recycling; Coll, collection; Rec, recycling. Yield losses at all life stages are indicated by dashed lines (in WM referring to landfills). When material is discarded to WM, it may be recycled (e), lost into the cycle of another metal (f, as with copper wire mixed into steel scrap), or landfilled. The boundary indicates the global industrial system, not a geographical entity (Recycling Handbook based on Graedel et al., 2011)


## End-Of-Life (EOL) Recycling Rate for 60 Metals

## Notes:

1. The figure uses the periodic table to show the global average end-of-life (postconsumer) functional recycling for sixty metals. Functional recycling is recycling in which the physical and chemical properties that made the material desirable in the first place are retained for subsequent use. Unfilled boxes indicate that no data or estimates are available, or that the element was not addressed as part of the study. These evaluations do not consider metal emissions from coal from power plants.
2. The End -of-Life (EOL) Recycling Rate (RR) relates to whatever form (pure, alloy, etc) recycling occurs.
3. Note that only 18 out of 60 metals are the EOL-RR values above 50\%, another 3 metals are in the $25-50 \%$ group and three more in the 10-25\% group.


Source: UNEP (2011b). Recycling Rates of Metals: A Status Report.
http://www.unep.org/resourcepanel/Portals/24102/PDFs/Metals_Recycling_Rates_110412-1.pdf

### 2.3.3 Plastics

- International trade in used plastics is prospering. With global production of plastics sky-rocketing, from 1.5 million tons in 1950 to 204 million tons in 2002 and 299 million tons in 2013, and a continuing shift of production from the West to Asia (more than $40 \%$ by weight of world production in 2013), the annual volume of transnationally traded waste plastics at 15 million tons represents just $5 \%$ by weight of new plastics production.
- Plastic scrap flows from Western countries with established recycling collection systems mainly to the PRC, which dominates the international market, receiving around $56 \%$ wt. of global imports. Europe (EU-27) collectively exports almost half of the plastics collected for recycling, at least $87 \%$ of which goes to the PRC.


Distribution of plastic applications in consumption and waste in the European Union.

### 2.3.4 Recycled Paper

Recycled paper and paperboard (known in the industry as 'recovered paper' or 'Recovered Cellulose Fiber' (RCF) has always been a major raw material used in the paper industry. In 1990, recovered paper accounted for $40 \%$ of the total pulp used in the European paper industry, and by 2013 this had risen to $53 \%$. At the same time total production in Europe had risen by around $50 \%$. This increase in 'recycled content' was driven mainly by the 'rediscovery' of municipal solid waste recycling and thus an increase in recovered paper supply, but the increase in MSW recycling rates from around $8 \%$ in 1990 to approaching $50 \%$ in 2012 meant that supply was outstripping regional demand.

- 'Collections' shows national totals of recovered paper and board collected by the secondary paper industry.
- 'Consumption’ shows national consumption of recovered paper by the paper industry (domestic deliveries plus imports)
- 'Net flows’ shows national consumption less national collections: a positive figure denotes a net importing country (highlighted in bold); a negative figure denotes a net exporter. These figures do not total exactly zero, as some stocks are carried forward between years. Note that some countries may be both a significant importer and a net exporter. Examples include the Netherlands and Belgium, where the ports of Rotterdam and Antwerp handle exports on behalf of a number of countries.


### 2.3.5 Textiles

Used textiles have become a globally traded commodity. Focusing on the second hand clothing economy in particular, this has doubled from 1.26 billion USD in 2001 to 2.5 billion USD in 2009. Textile recyclers sort clothing into reusable garments or recycling grades, the latter including industrial cleaning cloths and reclaimed fibers. The sector has globalized as a result of the growth of supply from the global North, the relocation of sorting operations to Eastern Europe and the global South, and the development of differentiated markets for reuse.

Five high-income countries (Canada, Germany, Republic of Korea, UK and U.S.) account for more than half of all exports of second-hand clothing, most of it originating as donations to charity when it reaches the end of its perceived useful first life. Charities typically select only a small percentage for domestic reuse (estimated at 20\% in the UK), often for sale in their own shops. The larger part is sold on to a complex network of global traders, being sorted many times into increasingly differentiated components. Major sorting centers are located in Poland, India and Ghana. Many of the higher quality garments are sold on in Eastern Europe. Lower quality wearable items from Europe and North America tend to go to Africa, while those from Asian countries tend to go to Asian markets (matching the clothing to the users body shape). Fifteen countries account for half of all imports: Angola, Benin, Cambodia, Cameroon, Canada, Germany, Ghana, India, Kenya, Malaysia, Pakistan, Poland, Russia, Tunisia and Ukraine Many of these countries are major re-exporters of sorted fractions.

### 2.3.6 Glass

The main source of glass for recycling is packaging, which accounts for $65 \%$ of the glass produced in the EU in 2014. On average, $70 \%$ of container glass is recycled in the EU, and new container glass uses $52 \%$ of glass cullet (crushed glass used as secondary raw material). Glass is mainly recycled as packaging and glass wool.
Recycling enables energy and cost savings in the production process. Because cullet melts at a lower temperature than raw materials, recycling can save around a third of the energy used in production. The by-products of the production process are usually re-used immediately. The recycling process needs glass cullet to be sorted by color (white or colored), either at source or after collection at extra cost, and to be clean of impurities such as labels, metal, ceramics or cork. Glass containing lead (e.g. lead crystal) must not be mixed with lead-free glass. The main challenges for glass recycling are that lead concentration tends to rise after consecutive recycling processes; and that flat glass, which accounts for $26 \%$ of European glass production, is under-used in recycling (both as a source and as a product of secondary raw material).

## Glass Recycling

جر اح مركز أجا - محافظة الدقهلية قرية متخصصة في ندوير الزجاج


### 2.3.7 E-Waste

A 2015 report by the United Nations University (UNU) estimated that 41.8 million tons (Mt) of e-waste was generated in 2014, almost 25\% more than the 2010 figure of 33.8 Mt . 2 The amounts of e-waste generated by type are shown in the figure .

Most of this waste was generated in Asia (16 Mt), followed by Europe (11.6 MT), North America (7.9 Mt), Latin America and Caribbean (3.8 Mt), Africa (1.9 Mt) and Oceania ( 0.6 Mt ). However, in e-waste generation per capita, Europe has the highest figure (15.6 $\mathrm{kg} /$ person) and Africa the lowest ( $1.7 \mathrm{~kg} /$ person).

Estimated annual generation in the coming years are as high as 50 Mt in 2018.


### 2.3.8 C\&D Waste

Construction and demolition (C\&D) waste is generated during the construction, renovation or demolition of buildings, roads, bridges, flyovers, subways, and so on. These activities typically generate large quantities of waste, although oftentimes data on C\&D waste are not collected routinely or consistently, so most published figures are estimates which need to be interpreted with caution. Such estimates include 8211 million tons of C\&D waste generated across the EU in 2012, 77 million tons in Japan, 33 million tons in China and 17 million tons in India (all in 2010), and almost 7 million tons in each of the fast developing cities of Dubai (2011) and Abu Dhabi (2013). C\&D waste often represents the largest proportion of total waste generated: for example, C\&D waste accounts for $34 \%$ of the urban waste generated within OECD countries. The volume of C\&D waste is also sharply increasing, reflecting the pace of infrastructure development across the world.

## Wood

Used for Animal Bedding, Mulch, Diesel Fuel, Electrical Power Plants and Particle Board
Bricks, Concrete and Other Masonry Products
Crushed and used for Fill, New Roads, Under lament for Concrete Applications
Metals (Ferrous and Non-Ferrous)
Melted into New Products
Roofing Shingles
Asphalt Roads
Cardboard
Processed used New Cardboard Products
Plastic
Made into bottles, floor tile, paneling, plastic lumber, etc.


### 2.3.9 Used Tyres Waste

The dynamic increase in the manufacture of rubber products, particularly those used in the automobile industry, is responsible for a vast amount of wastes, mostly in the form of used tyres, of which more than 17 million tons are produced globally each year. The widely differing chemical compositions and the cross-linked structures of rubber in tyres are the prime reason why they are highly resistant to biodegradation, photochemical decomposition, chemical reagents and high temperatures. The increasing numbers


Review
Progress in used tyres management in the European Union: A review
Maciej Sienkiewicz*, Justyna Kucinska-Lipka, Helena Janik, Adolf Balas


## Used Tyres Waste



| Waste Management 32 (2012) 1742-1751 |  |  |
| :---: | :---: | :---: |
|  | Contents lists available at SciVerse ScienceDirect | E |
|  | Waste Management | 1 |
| FISFVIFR | journal homepage: www.elsevier.com/locate/wasman |  |

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التنوير اليدوي لإطار ات الكاوتشوك في قرية ميت الحارون

### 2.3.10 Rare Earth Elements (REE)



Periodic table of the elements showing the division between LREEs and HREEs (Schuler et al., 2011).


Wikipedia photo $=$ Assortment of lanthanoide group el Uploaded at 22:12,19 April 2006 by User:Tomihhndor User:Tomihahndorf. Permission=GFDL.


Scandium
Wikipedia photo $=$ Gibe, free documentation license


Yttrium
Wikipedia photo $=$ To free documentation lic

## REE properties:

## Similar chemical properties

- Electropositive (valence 3+) - $\mathrm{Ce}^{4+}$ and $\mathrm{Eu}^{2+}$ also in natural systems
- Differ from other metals (Valence located in inner 4f subshell orbital, shielded by 5 s 2 and 5p6 outer closed (full) subshells)
- Stable outer shell results in very similar chemical properties and difficulty in their separation during processing
- Atomic nucleus is poorly shielded and with increasing atomic number, $4 f$ shell electrons pulled closer to the nucleus
- Reduction in the ionic radii with increasing ionic charge
- Lanthanide Contraction


## REE presence in Earth crust:

Abundance of Elements in the Earth's Crust

| Elements | Crustal Abundance (parts per million) |
| :---: | :---: |
| Nickel ( ${ }_{28} \mathrm{Ni}$ ) | 90 |
| Zinc (30 Zn ) | 79 |
| Copper (29Cu) | 68 |
| Cerium ( $5_{88} \mathrm{Ce}$ ) ${ }^{\text {a }}$ | 60.0 |
| Lanthanum (57La) | 30.0 |
| Cobalt (27 CO ) | 30 |
| Neodymium ( ${ }_{60} \mathrm{Nd}$ ) | 27.0 |
| Yttrium (39 Y) | 24.0 |
| Scandium ( 21 Sc ) | 16.0 |
| Lead ( $8_{2} \mathrm{~Pb}$ ) | 10 |
| Praseodymium (59Pr) | 6.7 |
| Thorium (80 Th) | 6 |
| Samarium (62 ${ }^{\text {Sm }}$ ) | 5.3 |


| Elements | Crustal Abundance (parts per million) |
| :---: | :---: |
| Gadolinium (64Gd) | 4.0 |
| Dysprosium (66Dy) | 3.8 |
| Tin (50 Tn) | 2.2 |
| Erbium (68Er) | 2.1 |
| Ytterbium (70 Yb) | 2.0 |
| Europium (63Eu) | 1.3 |
| Holmium ( 67 Ho ) | 0.8 |
| Terbium (6sTb) | 0.7 |
| Lutetium ( 71 Lu ) | 0.4 |
| Thulium (69 Tm) | 0.3 |
| Silver ( ${ }_{47} 7 \mathrm{Ag}$ ) | 0.08 |
| Gold (70Au) | 0.0031 |
| Promethium (61Pm) | $10^{-18}$ |

Lanthanides (lanthanoids), scandium, and yttrium are presented in boldface type.
(Adapted from Wedepohl, 1995)

## REE applications 1:

| Element | Applications |
| :--- | :--- |
| Scandium | Metal alloys for the aerospace industry. |
| Yttrium | Ceramics, metal alloys, lasers, fuel efficiency, microwave <br> communication for satellite industries, color televisions, computer <br> monitors, temperature sensors. Used by DoD in targeting and weapon <br> systems and communication devices. Defined by DOE as critical in the <br> short- and mid-term based on projected supply risks and importance to <br> clean energy technologies. |
| Lanthanum | Batteries, catalysts for petroleum refining, electric car batteries, high- <br> tech digital cameras, video cameras, laptop batteries, X-ray films, <br> lasers. Used by DoD in communication devices. Defined by DOE as <br> near critical in the short-term based on projected supply risks and <br> importance to clean energy technologies. |
| Cerium | Catalysts, polishing, metal alloys, lens polishes (for glass, television <br> faceplates, mirrors, optical glass, silicon microprocessors, and disk <br> drives). Defined by DoE as near critical in the short-term based on <br> projected supply risks and importance to clean energy technologies. |
| Praseodymium | Improved magnet corrosion resistance, pigment, searchlights, airport <br> signal lenses, photographic filters. Used by DoD in guidance and <br> control systems and electric motors. |
| Neodymium | High-power magnets for laptops, lasers, fluid-fracking catalysts. Used <br> by DoD in guidance and control systems, electric motors, and <br> communication devices. Defined by DOE as critical in the short- and <br> mid-term based on projected supply risks and importance to clean <br> energy technologies. |
| Promethium | Beta radiation source, fluid-fracking catalysts. |

## REE applications 2:



## REEs: Important Reference Material



## Rare Earth Elements' Processing;

Current and Emerging Technologies, and evolving needs within the Manufacturing Sector

SME (NYC)
October 18,, 2011
Jack Lifton
jacklifton@aol.com

## 3. The Biological Cycles WM Related Businesses



### 3.1 Biomass utilization in developed countries

- The European energy production from biogas reached 6 million of oil equivalent (Mtoe) in 2007 with yearly increase of $20 \%$.
- Germany has become the largest biogas producing country in the world. Number of biogas production units in operation is 7700 (2016) producing more than 8 billion cu m of biomethane as well as roughly the samr amount of "green" carbon dioxide per year (www.euroobserv-er.org).



## National Biomass Strategy: a Necessity

National Biomass Strategies and Action Plans, four examples:

- UK
- Germany
- Malaysia
- USA a billion ton annual supply target



### 3.2 Example of Related Resourceful Publications



### 3.3 Biomass to Bio-Power Pathway



Source: U.S. Environmental Protection Agency (EPA) State Bioenergy Primer (2009) http://www.epa.gov/statelocalclimate/resources/bioenergy-primer.html

### 3.4 Biomass to Bio-Fuel Pathway



### 3.5 Biomass to Bio-Products Pathway



Source: U.S. Environmental Protection Agency (EPA) State Bioenergy Primer (2009) http://www.epa.gov/statelocalclimate/resources/bioenergy-primer.html

## Case study: Spain Valorization of agro-business wastes

- The national Technological Center for the Canning and Food Industry (CTC) in Spain is implementing the "AGROWASTE" project in the Region of Murcia.
- AGROWASTE main objective is to help agro food companies in the valorization of organic wastes and by-products.
- AGROWASTE practical demonstrations focused on three directions:

1. Extraction of valuable compounds
2. Development of organic substrates for use in advanced agriculture industry
3. Production of energy by anaerobic digestion

Follows are three extraction examples:



## Valorization of garlic waste



## Unit Operations Applied in the Spanish Valorization projects

| code | Unit Operation | Description | Equipment |
| :--- | :--- | :--- | :--- |
| UO1 | Size reduction | Shredding, Crushing and Grinding <br> of solid materials | Shredders, Crushers, Grinders |
| UO2 | Extraction | Leaching with hot water or other <br> solvents | Extraction/leaching set-ups |
| U03 | Filtration | Solid separation from slurries using <br> different filter designs | Filters |
| U04 | Centrifugation | Solid-liquid separation by <br> centrifugation | Cenrifuges |
| U05 | Heating/Cooling | Heating/cooling of solutions and <br> slurries | Heaters, Coolers and Heat Exchangers |
| U05 | Evaporation | Concentration of solutions by <br> evaporation of solvents | Evaporators |
| UO7 | Drying | Solid-liquid separation by drying | Dryers |

## 4. Concluding Remarks

- There are many ways to present the Recycling Industry, one of which is to look at the "Technical Cycle" and the "Biological Cycle" related businesses.
- Each of the two cycles is linked to a big global industry with many subsectors included
- We have to understand different systems of "waste classification" and "waste definitions".
- Like all industries, the recycling industry has its "Best Practices", "Norms" and "Codes", " R\&D" and "Occupational Standards".
- Opportunities are tremendous !!!!

وختامـا...تحية واحترامـا للمدورين العظام في منشية ناصر ...!!!


## Annex: Recycling in the chemical industry

## Main source



## Welcome to The Essential Chemical Industry - online

This is a reference library of the world's principal industrial chemicals, their uses and their manufacture using current industrial processes and innovations. This new web-based edition was first developed in 2013 from the book of the same title, which went through five editions. It is intended for:

- school, college and university students and their teachers
- industrial chemists and employees of chemical companies needing a quick reference or overview


## About the The Essential Chemical Industry - online

Like the book was, The Essential Chemical Industry (ECI) - online is now one of the most highly respected and up-to-date resources about the chemical industry. This innovative website has easy cross-referencing and drill-down capability and achieves a new level of access for the student, researcher and industrial chemist alike. It has an exciting interactive research capability.

It is produced by Centre for Industry Education Collaboration (CIEC) formerly the Chemical Industry Education Centre, an independent non-profit organization in the Department of Chemistry, University of York, UK.

Written by members of the Centre's staff, and with the advice of over 200 experts in the field, the site is systematically reviewed and updated to ensure that it remains relevant and authoritative.

## How to use this site

You can simply dive in and enjoy a journey of exploration - OR you can research information with more precision. Follow the link for some useful tips on finding your way around the site.

## Recycling in the chemical industry

- Recycling of materials has become common practice over the last ten years or so, with households in many countries encouraged to save used cans, glass, plastics, paper and garden rubbish for special collection. These are then recycled for two main reasons.
- One is local, to save land which would otherwise be used as dumps for the waste. In the European Union alone, 1.3 billion tons of waste - some 40 million tons of it hazardous are thrown away annually. This amounts to about 3.5 tons of solid waste/capita. On top of this there is also a further 700 million tons of agricultural waste to dispose of.
- The other main reason for recycling has global significance - to help conserve valuable resources, such as metals, wood and energy.

This presentation is devoted to the recycling of metals, some basic chemicals and polymers, all within the context of the chemical industry.

## Recycling of basic chemicals

## Sulfuric acid

- Some sulfuric acid is produced from 'spent' (used) acid and related compounds such as ammonium sulfate which is a by-product in the manufacture of methyl 2methylpropenoate.
- The acid and compounds are usually in dilute solution which is evaporated under vacuum to produce concentrated solutions. These are fed into a furnace with oxygen at about 1200 K to produce sulfur dioxide:

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{SO}_{4} \longrightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{SO}_{2}+1 / 2 \mathrm{O}_{2} \\
& \left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}+\mathrm{O}_{2} \longrightarrow \mathrm{SO}_{2}+\mathrm{N}_{2}+4 \mathrm{H}_{2} \mathrm{O}
\end{aligned}
$$

- The sulfur dioxide is dried by passage through concentrated sulfuric acid. It is then oxidized to sulfur trioxide and hence sulfuric acid using the Contact Process.


## Recycling of basic chemicals

## Hydrochloric acid

- The steel industry is a major user of hydrochloric acid for the pickling process to remove impurities. The industry uses a process known as pyro-hydrolysis to recover the spent acid, which now contains a mixture of iron chlorides. The spent liquor is first concentrated in an evaporator, with dissolved HCl being given off and collected. The concentrated liquor is then fed into a roaster at ca $800-1000 \mathrm{~K}$ which converts the iron chlorides into HCl and iron(III) oxide, the HCl again being collected. For example:

$$
4 \mathrm{FeCl}_{2}+4 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2} \longrightarrow 8 \mathrm{HCl}+2 \mathrm{Fe}_{2} \mathrm{O}_{3}
$$

- HCl from both streams is absorbed in water to make $18 \%$ hydrochloric acid for reuse. It is difficult however to collect all the HCl gas, and emissions to air are a problem with this process.


## Recycling of basic chemicals

## Recycling within processes

- Many processes recycle reactants and products in order to conserve materials and make the processes as efficient as possible. An example is in the manufacture of chloroethene (vinyl chloride), the monomer for the manufacture of PVC. Chloroethene is made from ethene via 1,2-dichloroethane, which is then cracked:

- The hydrogen chloride is recycled and reacted with oxygen and more ethene. The overall reaction can be represented by:

$$
\mathrm{CH}_{2}=\mathrm{CH}_{2}(\mathrm{~g})+\underset{\substack{\text { recycled } \\ \text { hydrogen chloride }}}{2 \mathrm{HCl}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{ClCH}_{2}-\mathrm{CH}_{2} \mathrm{Cl}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})}
$$

## Recycling of polymers

- The world's annual production of plastics is nearly 300 million tons. China accounts for about $24 \%$, and the rest of Asia another 16\%, Europe $20 \%$ and NAFTA (North American Free Trade Agreement: US, Canada and Mexico) another 20\%. To put these numbers in perspective, 20000 large bottles can be made from just one ton of plastic. Further, the plastics industry uses nearly $5 \%$ of the world's oil supply.
- One of the great problems facing the industry is to ensure that the plastics can be recycled.


## Recycling of polymers Cont.'d

Annual production of plastics 2012

| China | 57.6 million tons |
| :--- | ---: |
| Rest of Asia | 38.1 million tons |
| NAFTA | 48.0 million tons |
| Latin America | 11.8 million tons |
| Europe | 49.2 million tons |
| Russia* | 7.2 million tons |
| Middle East \& Africa | 17.4 million tons |
| Japan | 11,8 million tons |

*Russia plus Commonwealth Independent States that used to be part of the Soviet Union

## Recycling of polymers Cont.'d

## Reusing plastics

- Reusing plastics would be ideal, and already happens for example, with bottle crates and increasingly with shopping bags. At first sight, collecting plastics which can be remolded, for example the thermoplastics, such as poly(ethene) and poly(propene), would appear to be an attractive solution. However, collecting and sorting plastic articles into specific polymers is an expensive and difficult process. It is often done manually by trained staff who sort the plastics into polymer type and/or color. Technology is being introduced to sort plastics automatically, using various spectroscopic techniques.
- First, infrared spectrometry is used to distinguish between clear and translucent plastic. Next a vision color sensor, programmed to ignore labels, identifies various colored plastics. X-ray spectrometry is then used to detect the Cl atom in poly(chloroethene) (PVC). Finally a near infrared spectrometer is used to detect resin type, most importantly for the separation of high density poly(ethene) (HDPE) and a polyester such as PET. Typical sorting rates are of the order of 3 items per second.


## Recycling of polymers Cont.'d

## Reusing plastics Cont.,d

This machine sorts bottles and other containers made from different polymers prior to cleaning and shredding. It distinguishes between different polymers using a NIR (near infra-red) detector. This distinguishes between bonds in a molecule. There is also a separate detector which allows metals to be removed.


## Recycling of polymers Cont.'d



## Recycling of polymers Cont.'d

## Reusing plastics Cont.,d

- Plastic can also be separated on the basis of density by flotation. One recently developed method involves spreading the plastic and passing it through a series of pipes in suspension in water. The flow rate of the plastic depends on the density, enabling streams to be taken off at different points along the pipe.
- Recycling of polyesters, for example PET (in bottles), is now widely used. The recovered bottles are washed, ground into flakes, melted and extruded as fibers. The fibers are then used to make products such as carpets.
- High density poly(ethene), HDPE, used for juice and milk bottles, is also ground into flakes, melted and pressed into sheets to be made, for example, into bin-liners or molded into containers.
- Recycling of plastic bags saves about two thirds of the energy used to produce a new bag. PVC is similarly recycled and extruded for pipes or used for window frames.


## Recycling of polymers Cont.'d

## Converting polymers into monomers

- Some polymers can be depolymerized to reform monomers, which can then be purified by distillation and polymerized again to produce the polymer. This still has the drawback that the polymer waste has to be sorted prior to being heated.
- For example, PET waste is dissolved in the dimethyl ester of benzene-1,4-dicarboxylic acid (dimethyl terephthalic acid) and then heated with methanol under pressure at 600 K. This produces the two monomers of PET, ethane-1,2-diol and the dimethyl ester which are subsequently purified by distillation


dimethyl ester of
benzene-1,4-dicarboxylic acid

$$
+\mathrm{nHO}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{OH}
$$

## Recycling of polymers Cont.'d

## Converting polymers into monomers Cont.,d

- Polyamide 6 (nylon 6), used in carpets, is converted back to its monomer, caprolactam. The backing is removed from the carpet and the carpet is then shredded and pulverized. On heating, polyamide 6 depolymerizes:

polyamide 6

caprolactam
- After purification, by distillation, the monomer is polymerized again to yield polyamide 6. In another process, it is not necessary to remove the backing (which is an added expense). Instead, the polyamide 6 fibers are heated in a stream of superheated steam and depolymerized.


## Recycling of polymers Cont.'d

## Cracking the polymer

Polymers, like other high molecular mass organic compounds such as the alkanes in oil, can be cracked at high temperatures to form smaller molecules. For example, if they are steam cracked, polymers such as poly(ethene) and poly(propene) yield alkenes and alkanes of small molecular mass which can be used in the same way as those formed in the cracking of naphtha. Small cracking plants are being built for this purpose.

## Recycling of polymers Cont.'d

Cracking the polymer Cont.,d

This yacht is using sails made from recycled poly(ethene).


## Recycling of polymers Cont.'d

## Cracking the polymer Cont.,d

- Mixtures of polymers can be converted into useful compounds either by pyrolysis or by oxidation. This has the advantage that the plastics do not have to be rigorously sorted before being treated. The mixture of polymers is heated in a stream of hydrogen at about 500 K . If the polymers contain chlorine (for example, PVC), hydrogen chloride is formed and is washed out. The remaining gases are then heated at about 700 K and cracked to form the usual mixture of hydrocarbons (alkanes, alkenes, aromatics) which can be fed into the stream of hydrocarbons formed from the steam cracking of oil fractions.


## Recycling of metals

- The recycling of metals (often referred to as secondary production) is becoming increasingly important with more aluminum and lead being produced from recycled sources than from their ores, and vast quantities of steel and copper also being produced via recycling.
- In all cases the properties of the metals following recycling are completely unimpaired. Their quality is just the same as for metal produced from the ore.
- The materials for recycling come from three sources. One is the waste material generated by the initial manufacture and processing of the metal. Another is waste material from the fabrication of the metals into products. Both of these sources are referred to as new scrap. The third, most commonly regarded by the public as recycling, is the discarded metal-based product itself (old scrap). Thus in manufacturing a car, each of the three sources of recyclable metal becomes available from the steel mill itself, from the factory making the cars and lastly when the car itself is eventually recycled.


## Review Questions

1. Recycling is a big industrial business. Discuss the following topics:
a. Recycling rate of different materials
b. Waste sources and definitions
c. Rare Earth Elements (REEs)
d. Recycling of used tyres
2. Draw a neat diagram/table to show your understanding of each of the following topics:
a. The technical cycle in the Ellen MacArthur Foundation circular economy model
b. The biomass to bio-products pathways
c. The valorization of onions waste as per the Spanish agro-industry experience
d. Unit operations applied in the Spanish agro-waste valorization project

[^0]:    Source: Ellen MacArthur Foundation (2013) (http://www.ellenmacarthurfoundation.org/circular-economy/circular economy/interactive-system-diagram).

