1. GREEN CHEMISTRY

1A. WHAT IS GREEN CHEMISTRY, AND WHY DO WE NEED IT?

Chemical manufacturing- under pressure

- Consumer demands:

- More sophisticated materials
- Safer pharmaceuticals and agrochemicals
- New products
- Low cost

Environmental demands:

- No environmental impact
- Products to be recyclable
- Safer processes and plants, avoiding use of hazardous materials
- "What price our children's future?"

How did we get here? (1)

Traditionally academics focused only on lab scale synthesis, without any regard for the environment. When their methods were scaled up, inefficient processes and toxic waste were the result.

Example: Manufacture of 1 tonne of a typical pharmaceutical produces 50 tonnes of waste.

How did we get here? (2)

Meanwhile, in industry, chemists are dependent on academic methods (with "tweaking") for most of their processes.

- The timeframe for process development (typically 1-2 years maximum) precludes the development of totally new methods.
- With a customer reliant on a fixed delivery date, it is far too risky to experiment with totally new ideas.

1B. GREEN CHEMISTRY SOLUTIONS

Traditional solutions

- Dilute waste in the ocean or river

  "Dilution is the solution to pollution"
- Make simple changes to the process to make it "greener"

  Example: replace benzene (very toxic) with toluene (much less toxic)
- "Tailpipe treatment", i.e. hazardous waste is treated at the plant to make it safer

  Example: A scrubber on the smokestack

Problem: all of these treat the symptoms (waste) rather than the cause (waste production)

Is there a better solution?

- *Sustainable Development-*

  Continued economic growth and development, but not at the expense of the environment. All activity must be sustainable- i.e., it must have no net impact on the environment.

What we want from manufacturing:

Cheaper
More products
More advanced

MORE

Safer
Less pollution
Use fewer resources

FROM LESS

What we need…..

Cheaper

More products

More advanced

Safer

Less pollution

Use fewer resources

….is green chemistry!

GREEN CHEMISTRY

US EPA

http://greenchemtech.blogspot.com/

Green chemistry

- Design of chemical products and processes that are "benign by design," so as to prevent pollution.
- Focus on pollution prevention rather than end-of-pipe control.
- Uses chemical principles such as catalysis.
- A related field is "green engineering:" this uses engineering principles to achieve the same goals.

Green Chemistry: definition

"Green Chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, by-products, solvents, reagents, etc., that are hazardous to human health or the environment".

Paul T. Anastas & Tracy C. Williamson, in "Green Chemistry", ACS Synposium Series 626, 1994

Twelve principles of green chemistry

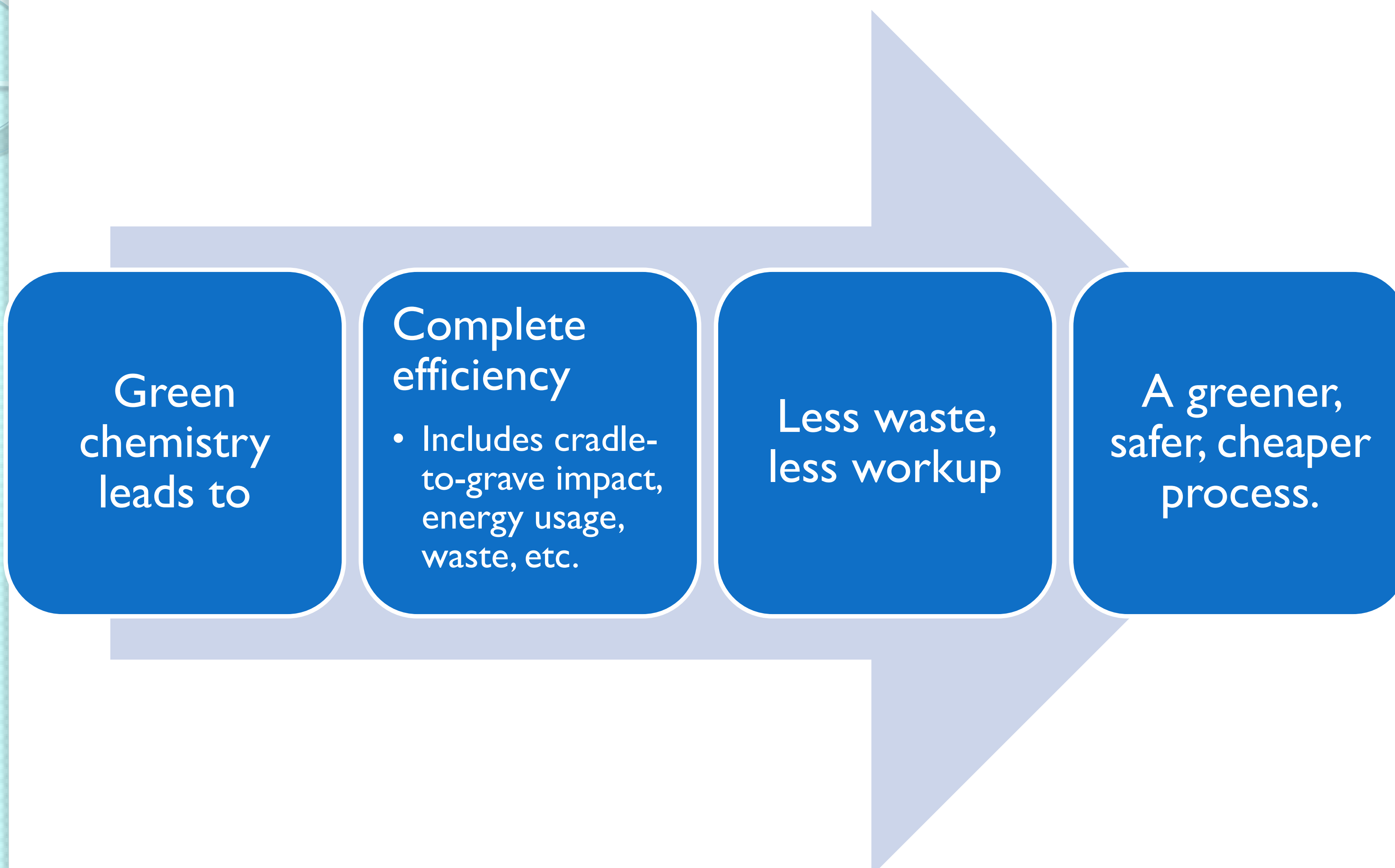
- Prevent waste
- Design safer chemicals and products
- Design less hazardous chemical syntheses
- Use renewable feedstocks
- Use catalysts, not stoichiometric reagents
- Avoid chemical derivatives
- Maximize atom economy
- Use safer solvents and reaction conditions
- Increase energy efficiency
- Design chemicals and products to degrade after use
- Analyze in real time to prevent pollution: Minimize the potential for accidents

Green chemistry is not

- Environmental chemistry
- Cleaning up the waste after you've made it (tailpipe treatment).
- Focusing on one aspect alone such as a solvent, while ignoring the whole picture.
- Perfect!

NY City Dept. of Sanitation Picture from Flickr, by Salim Virji, CC license

The result


Green chemistry leads to
Complete efficiency
• Includes cradle-to-grave impact, energy usage, waste, etc.
Less waste, less workup
A greener, safer, cheaper process.

The result

- More truly efficient

The result

- More truly efficient
- More efficient = much less waste

By Guillaume Paumier, Wikimedia Commons, CC License

The result

- More truly efficient
- More efficient = much less waste.
- More efficient = more profitable!

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IC. GREEN CHEMISTRY IN PRACTICE

Life-cycle assessment

- Follow the product from cradle to grave:
  - Use of resources (materials and energy)
  - Emissions & waste, also by-products & energy released
  - All steps in making the product
  - Disposal- to be recycled or biodegradable
- Applicable to all manufactured products, such as cars, diapers, etc.

Four basic components

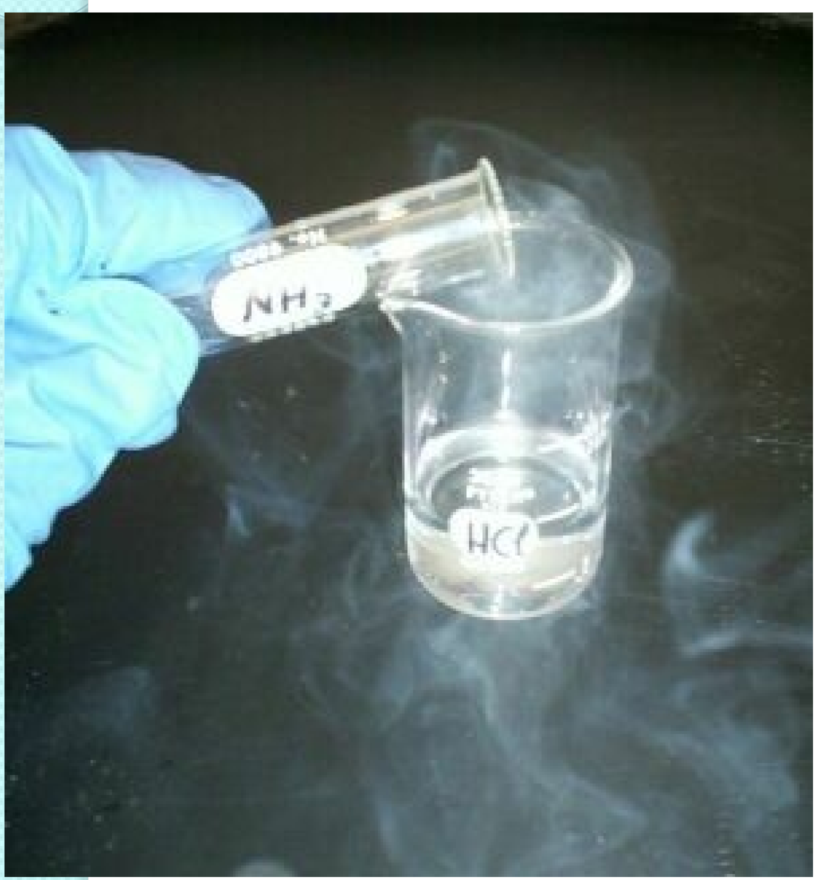
1. Nature of the Feedstocks or Starting Materials, and of Reagents
2. Nature of the Transformations

   May consider a single step, or all steps together

3. Nature of the Reaction Conditions
4. Nature of the Final Product or Target Molecule

NOTE: All of these are closely related, sometimes inextricably.

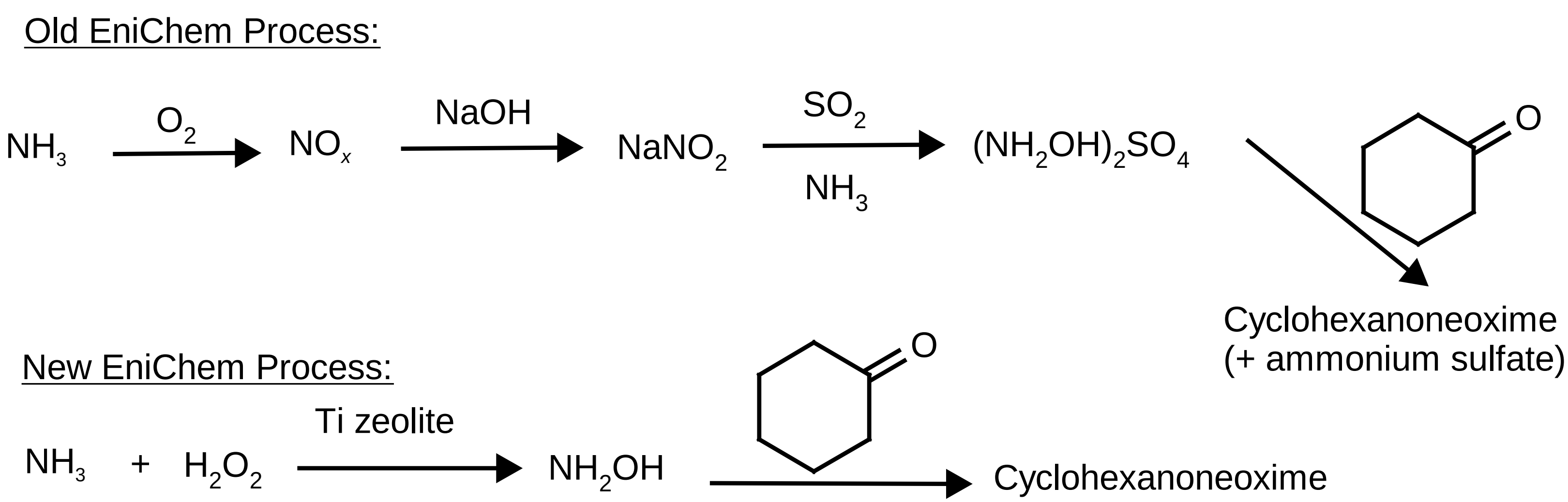
1. Starting Materials and Reagents



- Should be environmentally benign
- Ideally should be cheap, and from sustainable sources

1. Starting Materials & Reagents

- Example: Cyclohexanoneoxime production
  - The old process uses several toxic & hazardous reagents. The new process replaces all of these with nontoxic reagents – and makes the process simpler & shorter!



2. The Transformations

- Synthesis design (for all steps together):
  - Reducing the number of steps can have a big effect on reducing waste, because of cumulative effects

Example:

  - Original route to ibuprofen involved six steps, none of which used catalysis
  - Modern route involves only three steps, all of which use catalysis

- Often assessed by E-Factor (Sheldon)

$$\textit{E-Factor} = \frac{\textit{mass waste produced}}{\textit{mass of product}}$$

2. The Transformations

One way to measure "greenness" of a single step:

- Atom Economy

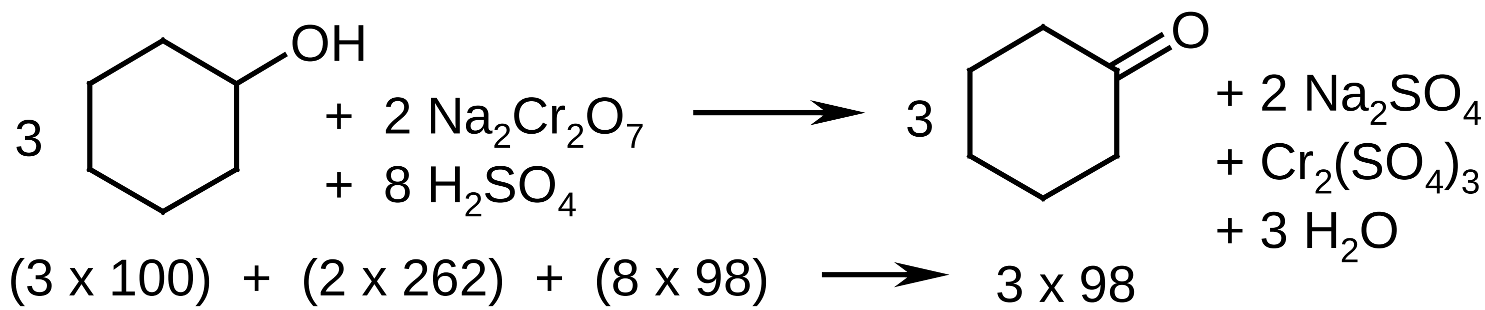
Defined as

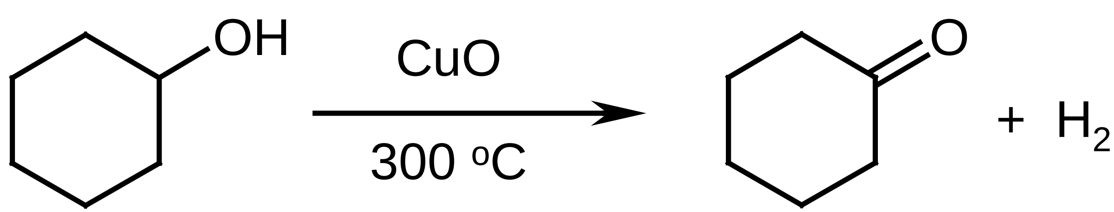
$$\%\ \text{Atom economy} = \frac{\text{mass } \textit{desired} \text{ products made}}{\text{mass of all reactants used}}$$

This is a theoretical calculation, assuming the yield is 100%; it represents the maximum attainable in practice. Based on idea that any mass not used to make product must end up as waste.

Atom economy

Numbers show the numbers & masses of each molecule, used in the calculation. The traditional process shows only 18.3% atom economy, but the “green” process has 98% atom economy. So 100 lb of starting materials would lead to 98 lb of products!





Traditional: Jones oxidation $K_2Cr_2O_7$ & H_2SO_4

Produces toxic Cr(VI) waste. AE = 18.3 %

"Green": Remove hydrogen as H_2, requires heat. AE = 98%

3. Reaction conditions

- Use of catalysis
- Use of benign solvents
- Use of conditions that allow product to be easily isolated & purified
- Low energy processes

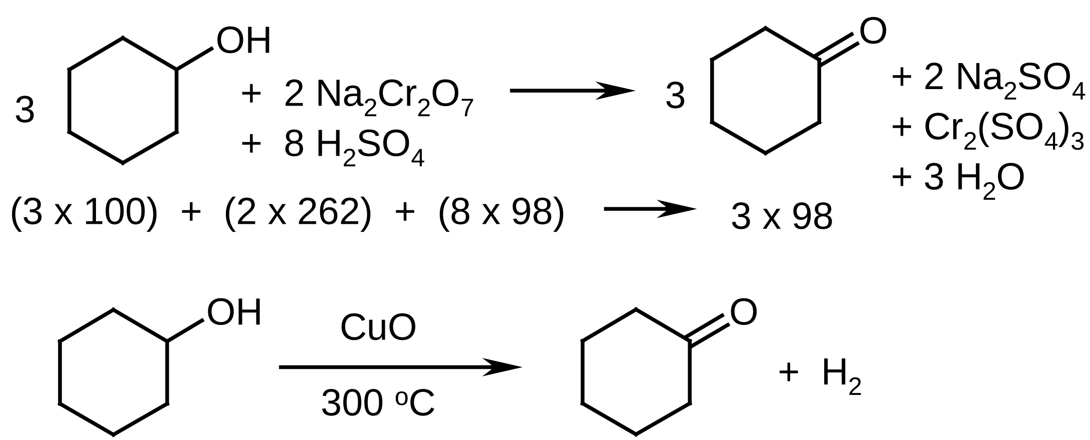
Note: Introduction of any of these features will usually result in a cheaper, more efficient process- very attractive to industry!

3. Reaction conditions: Catalysts

- A catalyst speeds up a reaction without being consumed. Need only a small amount.
- It may allow a process to be run with less heat, or to make a product with less waste.
- Alternatively, it may allow one product to be made selectively

3. Reaction conditions

- Catalyst: speeds up the reaction rate without being consumed.
  - Usually only need small amounts, recyclable
- See atom economy example from above, shown below – the “green” process uses catalysis (by copper(II) oxide), the dirty process doesn’t.



Traditional: Jones oxidation $K_2Cr_2O_7$ & H_2SO_4

Produces toxic Cr(VI) waste. AE = 18.3 %

"Green": Remove hydrogen as H_2, requires heat. AE = 98%

3. Reaction Conditions

- Use benign solvents, such as water or supercritical carbon dioxide

WATER

Problem- many things don't dissolve. May need to make new catalysts that will take materials into water.

sc CO_2

Problem- need pressure/special equipment. However commercial processes have been developed, e.g. for hydrogenation (as used in ibuprofen synthesis).

3. Reaction condition: Benign solvents

Supercritical carbon dioxide can replace toxic chlorinated solvents for dry cleaning or (as here) decaffeination of coffee

- Traditional organic solvents are often hazardous and damaging to the environment.
- If possible, avoid using solvents altogether, or use water.
- Another benign alternative is supercritical carbon dioxide.

3. Reaction Conditions

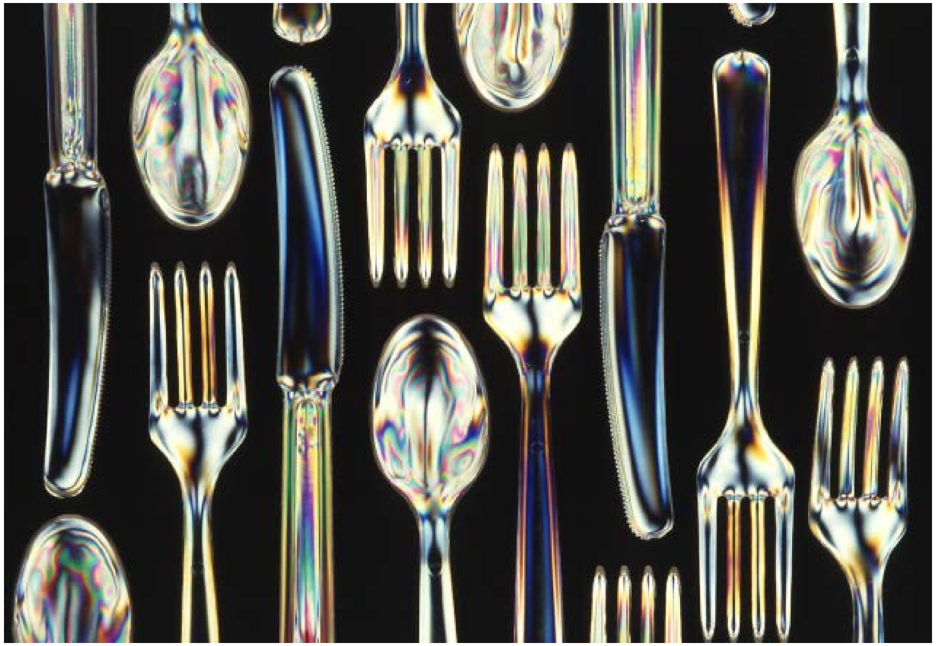
- Ease of isolation/purification
  - This (often overlooked) aspect is usually the most lengthy part of a process. Frequently many extra materials are used here, and much more waste generated
- Reduced energy usage
  - Low temperature processes (ideally room temp.)
  - Short processes are good!

4. Final product: Fighting fires

"Pyrocool" is a safe biodegradable material for fighting major fires

- Design a product (final molecule) that is environmentally benign
  - Non-hazardous
  - Non-toxic
  - Biodegradable

4. Final product: Bioplastics



- These utensils are made from a combination of starch and polyester. They are also biodegradable.
- Starch makes up about half of the carbohydrate you eat. Why use up petroleum when we can use biowaste instead?

Picture by US Dept. of Agriculture

Detergents

- Post-war detergents used branched chain alkylbenzenesulfonate salts that were not biodegradable.
- Modern detergents use straight chain salts that degrade much more rapidly.

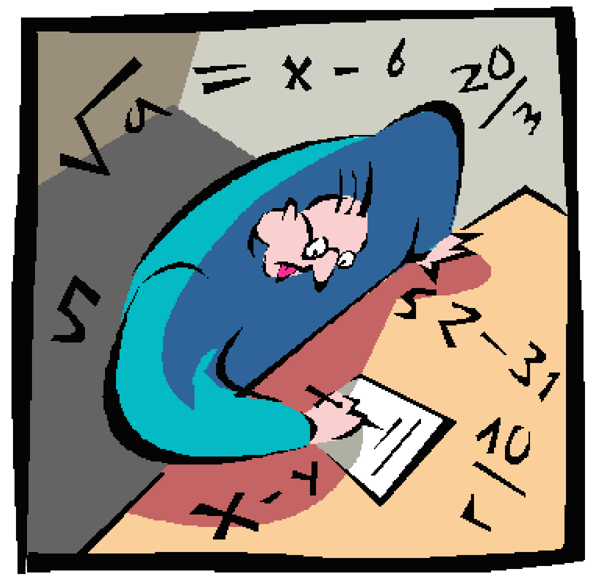
This older picture shows a bridge in Brazil, where the old-style detergents had made the water in the river frothy, requiring a permanent spray to keep the foam down.

Saving the ozone layer

- Chlorofluorocarbons (CFCs) were heavily used in aerosols and as refrigerants until around 1990.
- Although very safe & non-toxic, CFCs destroy ozone in the upper atmosphere that protects us from harmful UV rays.

Saving the ozone layer

- In 1987 the Montreal protocol was passed, banning production of CFCs after 1995, and phasing out use of CFCs.
- Chemists needed to design safe, cheap alternatives- ***FAST***!
- Very quickly, new replacements such as hydrofluorocarbons were developed.
- Some replacements have very low ozone depletion effects, other have zero effect.



2. GREEN ENGINEERING

2.1. Green Engineering- an overview

"Green engineering is the design, commercialization, and use of processes and products, which are feasible and economical while minimizing

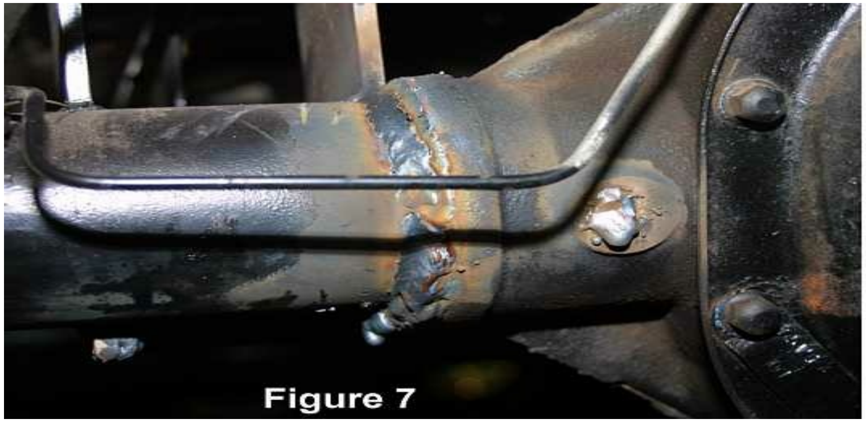
1) generation of pollution at the source and
2) risk to human health and the environment."

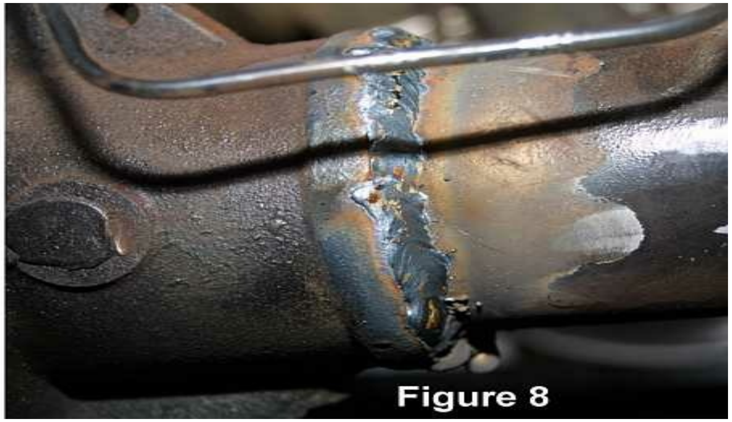
http://www.epa.gov/oppt/greenengineering/whats_ge.html

[Note emphasis on WRAS = Waste Reduction At Source]

Green Engineering

Typically green engineers use a combination of experience and theoretical modeling in order to estimate exposure & releases of toxic materials.





This pipework is leaking…..

Green Engineering

By applying risk assessment concepts to processes and products, the engineer can accomplish the following:

- **estimate the environmental impacts** of specific chemicals on people and ecosystems;
- **prioritize chemicals** that need to be minimized or eliminated.
- **optimize design** to avoid or reduce environmental impacts;
- **assess feed and recycle streams based on risk** and not volume within a chemical process.
- **design "greener" products and processes**.

Possible environmental impacts: Resources & nature

- Impact on resources
  - Use of non-renewable resources
  - Use of renewable resources
  - Pollution of resources
- Direct impact on nature & landscape
  - Loss of nature
  - (Negatively perceived) change in landscape

Possible environmental impacts: Pollution

- Air pollution
  - Global warming
  - Ozone layer
  - Toxics in ambient air
  - Smog
  - Acid rain
  - Smells
- Miscellaneous
  - Noise
  - Ionizing radiation
- Soil pollution
  - Solid waste added
  - -> Eutrophication
  - Toxics added to soil
  - -> groundwater pollution
- Surface water pollution
  - Biol. or chem. oxygen demand
  - Toxics
  - Warming of surface
  - -> Eutrophication

Hazard Assessment

Risk = (Size of Hazard) x (Chance of accident)

2.2. Green Engineering- Products

SCREENING OF PRODUCTS:

- Use sustainable resources
- Life-cycle assessment
- Design the product to be more sustainable in use
- Design the product for re-use/recycle

Methods of life-cycle assessment

- Qualitative
- Quantitative
- Often a simplified version is adequate if choices are obvious
- Checklists
- Focus on continual improvement

Note that many parts of any LCA involve subjective judgment

2.3. Green Engineering- Processes

ORGANIZATION: Need the following, all of which require a lot of effort!

- Collaboration to design clean processes
- Full-cost accounting of waste costs
- Genuine commitment by management and the workforce
- Access to knowledge of clean technology

Methods for waste minimization in manufacturing processes

- “Housekeeping” measures
- Improved technology
- Proper cost analysis- see the paper mill example below
- Analysis of the full production chain

Example 1: Pesticides Plant Housekeeping

Source of waste problem	Waste prevention option
Off-specification product	Input & process control Reprocessing
Material losses/emissions during handling	Minimize handling
Activities (spills, leakage, remnants in packaging & processing equipment	Enclosure of the production system
Rinse waste from cleaning	Compatible cleaning agent- added to next batch
Filter waste	Avoid contamination through good input handling Change of filter media Improved process control

Example 2: New technology at a paper mill

Steps in Paper Production	Current Advanced Technology	Improved Technology
Slushing	Incl prewetting/improved stirring	Pulping at high consistencies
Disperging		Kneading at low temp. with high consistency
Sheet forming	Formation wire	Gap former/high consistencies
Internal water treatment	Conventional scrubbing & floating	Membrane supported scrubbing & floating
Press draining	Conventional press	Impulse drying
Thermal drying	Optimized cylinder-drying	Press drying

Example 3: Paper mill costing

Waste prevention option	Simple payback time according to company (years)	Omitted private costs or benefits	Revised simple payback time with full private costs (years)
Fiber, filler & water re-use on two machines	4.2	Wastewater pumping & treatment, fresh water treatment	1.6
Coating of paper- aqueous instead of solvent/heavy metal	7.6	Heating necessary to prevent freezing & to dry coating	11.7

Ways to improve the process

- Go from open process (much outflow) to closed process
- Reduce human intervention to reduce failure rates
- Continuous instead of batch process
- Change the nature of the process itself
- Change inputs to the process (incl re-use)

References

- L. Reijnders, *Environmentally Improved Production Processes and Products: An Introduction*, Kluwer, Dordrecht, 1996.