

THE INSTITUTION OF ENGINEERS, AUSTRALIA
AUSTRALIAN INSTITUTE OF HEALTH SURVEYORS
W.A. DIVISIONS

CONFERENCE

Waste Management

PERTH, W.A.

JULY, 1977

RE-CYCLING - POTENTIAL OF AVAILABLE TECHNOLOGIES

A. F. M. Barton
Senior Lecturer in Chemistry,
School of Mathematical and Physical Sciences,
Murdoch University, W.A.

RECYCLING - POTENTIAL OF AVAILABLE TECHNOLOGIES

Allan F.M. Barton, School of Mathematical and Physical Sciences,
Murdoch University

Introduction

Primitive societies recycled materials to a considerable extent because labour was more readily available than materials: garbage was fed to animals, containers were all reusable, and tools were always repaired. Consideration of energy and entropy factors show that waste recycling problems are inevitable, and a compromise must be reached between material conservation and energy expenditure. There always will be materials recycling problems, but the sooner we face them the less critical they will be.

Modern society, in emphasizing disposal rather than salvage and recycling, has tended to use methods of waste treatment that are even more primitive than those practised early in man's development: burning, burying, or dumping in rivers and seas. There has been much recent interest in advanced incineration and compaction techniques, where *disposal* is the primary aim.

Modern society operates by using *energy* to turn *resources* into *waste*, and of this trio of problems, *waste* receives even less attention than energy and resources. Exponential growth of the waste problem in our affluent, throw-away society now makes it obvious that recycling should be the goal, and it is therefore necessary for scientists and technologists to examine all aspects of fabrication and processing techniques to facilitate the reuse of materials. The philosophy of recycling provides a new set of priorities, and it is my aim here to consider various recycling processes in the light of the associated chemical and physical properties of materials.

The need for recycling is most apparent in a small, completely isolated system, demonstrated dramatically in the manned lunar expeditions. For example, hydrogen and oxygen for fuel cell power were "recycled" to provide drinking water. The space programme has had the highly beneficial effect of causing man to look at his planet as a spaceship,

emphasizing the importance of recycling at all levels. Nevertheless, the great technological achievement of moon landing was accompanied by astronauts dumping their refuse on the moon in the time-honoured terrestrial manner. Despite the prospects promised by science fiction, it is unlikely that we can import from outside the planet any appreciable quantity of materials.

In order to clarify and systematize recycling and pollution problems, it is helpful to consider a hierarchy of systems ranging from an atom to the Universe. At all levels lower than the Universe there is a theoretical upper limit to the effectiveness of recycling. It is possible that at this level, the Universe is in fact a perpetual motion machine, the only system capable of complete containment of its given energy and matter. Certainly at all lower levels, material can never be fully recycled, and any recycling requires the expenditure of energy.

When the recycling of a particular material is considered, it is necessary to decide on the level at which the problem should be tackled. For example, although glass bottles are discarded all over the world, the chemical constituents of glass are not in short supply. Indeed, it has been estimated that if everyone on earth continually drank beer and discarded the empties forever, geologic processes would turn the empties back into sand before we ran out of it for making more bottles. Here the main problem exists at the city or state level. Discarding tinned steel cans is another matter: many materials such as tin are in short supply on the planet scale. Except for the loss of gases such as hydrogen and helium from the top of the atmosphere, material is essentially conserved on Earth, but recycling involves not only conserving a particular element but also preventing it from becoming disseminated throughout the earth's crust and biosphere.

These examples illustrate the importance of *time* in recycling decisions. Another example may be of value here. In the construction of accommodation we can recognize three distinct time scales:

- (i) that of the speculative builder, one or two years;
- (ii) that of the average house owner, who looks forward 10 or 20 years and provides maintenance to protect the materials before "recycling" becomes necessary;
- (iii) that of society as a whole, concerned with depletion of forests and energy reserves, and with optimum land use.

Short time scale considerations in the long run involve greater energy and resource costs than long term planning, although the initial and apparent costs of the latter may be greater.

If elements are considered to be the components being recycled, all pathways are cyclic except those involving nuclear reactions. More often, however, the aim is to preserve groupings of atoms with particular useful characteristics or high potential energy values: at the moment there is little practical advantage in recycling carbon as carbon dioxide from the oxidation of fuels. This introduces the subject of energy because in each process it is usual for energy to be expended. A balance must be achieved between expenditure of energy and conservation

of material. If the material is extremely rare, no energy cost is too great. Extensive recycling occurs only when economically justified, and economic conditions depend on both supply and demand. The balance is shifting as supplies dwindle and demand grows: more and more materials now justify the expenditure of energy and effort necessary for conservation.

The various types of recycling can be summarized as follows, listing the possibility in approximate order from the most preferred to the least preferred.

Categories of recycling

Types of recycling	Examples
Re-use of article	Returnable, refillable bottle
Non-sacrificial recycling: re-use of material at similar quality level	Colour-sorted glass cullet Newspaper repulping for newsprint production
Non-sacrificial recycling: re-use of material at lower quality level	Roofing felt from waste paper Fibreglass insulation from bottles
Sacrificial recycling: new use of material	Road paving material from glass Composting of paper
Conversion of storable fuel	Pyrolysis of urban waste
Direct incineration to produce energy	Incineration of urban waste

Separation

Before a material is processed for recycling it is usually necessary to separate it from a variety of other materials. This process of separation opposes the natural tendency to increasing disorder and so always requires the expenditure of energy. Materials have many unique physical and chemical properties which may be applied in separation processes, ranging from colour, density and texture utilized subconsciously in manual sorting, to magnetic properties which require chemical equipment.

Separation problems may be chemical or physical. This is exemplified by copper: although copper has a relatively high intrinsic value, it is estimated that only about 60% of the available waste copper is recycled. One reason for this is that in electric motors copper windings are usually surrounded by a far greater mass of iron (a physical separation problem); another reason is that a considerable proportion of the copper is used as brass, recycling of which is often found to be uneconomical (a chemical problem).

If physical separation is possible, this is preferable to chemical separation which usually requires large inputs of energy, chemicals and technology.

Some materials are by their very nature dissipated widely: titanium recycle potential is small, since 90% of the titanium currently used is dispersed as titanium dioxide pigment. Zinc (on galvanized iron) and tin (on tin plated cans) are further examples.

In some cases a new technological development makes an apparently difficult separation feasible; cryogenic separation of wire from rubber or plastic (in waste cable and tyres) is a good example.

Many of the problems which are at present encountered could be avoided by improvements at the design stage. For example, incorporation of iron compounds in polymer beads used as filter aids (a substitute for diatomaceous earth) facilitate separation and washing: the magnetic characteristics permit the beads to be gathered up and washed, or they can be shaken in alternating magnetic fields so that the dirt is dislodged. This technique obviously has considerable potential in other fields; in the future some method of coding incorporated in all plastics during manufacture may assist separation in the waste stream.

It may prove necessary to substitute materials to improve separability for recycling. Thus copper as an impurity in steels is often detrimental because it reduces formability and the copper wiring in cars makes the recycling of the steel more difficult. Although aluminium presents some problems in making reliable electrical connections, in the long run it may be preferable to use aluminium wiring in cars.

If a manufacturer is not responsible for recovering his own products, economic factors alone will not promote this type of rationalization, and ease of separation of components for recycle will have to be under legislative control along with the present purity or design standards and quantity or quality specifications.

Physical Separation

Hand sorting, although labour intensive and costly, is still widely used in salvage industries. It ranges from simple hand-picking of urban waste to sorting textiles, removing impurities from recycled paper, and determining the composition of alloys and plastics with the aid of physical and chemical tests. This is the "Maxwell demon" approach to recycling. (Maxwell invented the "demon" in 1871, a mythical being of molecular size who could separate fast-moving from slow-moving molecules). Entropy (disorder) of mixing is overcome by human endeavour with a relatively small expenditure of energy. Thus in most factories and workshops it would be possible with a little organization to keep different kinds of scrap metals separate.

The emphasis in the future, however, will be on mechanical separation, because it is only by the application of modern automated techniques and scientific research that significant progress will be made in resource recycling.

Any sorting operation always involves a prior coding or identification process. In some cases coding is simple, as in the magnetic separation of ferrous from non-ferrous metal. More often, it is necessary to deal with multi-component items, for example a beer can with tinned steel body, aluminium ends, and a paper label. Here there are two possibilities. One is to use several sensors observing and measuring different properties, as a human sorter would, and come to a conclusion about the nature of each item. The second is to grind or shred everything so finely that most individual particles are homogeneous, and then separate them. This second alternative has the disadvantage that we give up the "order" and concentration of material that already exists, and then have to build it up again from a much more disordered level.

In a magnetic separating operation, coding and sorting take place at the same time. This is not usually the case, but the response to other physical properties (e.g. colour) of a sensor (e.g. a beam of light) can operate a switch to divert items by conveyor belt or air blast to the appropriate hopper.

The first stage in the development of automation from manual "picking" of waste is to use manual coding and machine switching: a human coder operates the controls of a mechanical separator. The next stage is complete automation, and the mechanical coder/separator which most closely approximates to manual sorting is an urban waste sorting machine being developed for larger items of waste at the Massachusetts Institute of Technology. A computer examines data from several types of sensor (metal detector, impact sensor and infrared sensor) and determines a category for each individual item. This technique is still in the development stage, but could well complement the shredding, sieving, winnowing and slurring processes now in use for recovery from urban waste. In conjunction with this sorting system, a detailed survey has been carried out of the size characteristics of urban waste. It appears that sorting by size alone affords a method of preliminary concentration of the various components.

In a few favourable cases materials have unique characteristics which facilitate separation, such as ferromagnetism in the case of iron. More commonly, however, materials exhibit a range of properties in any physical or chemical characteristic, and it is necessary to develop a separation process based on variation of density, solubility, etc.

Magnetism has been used for many years in drum and belt separators for mineral beneficiation, impurity removal, and scrap metal sorting. The permanent magnet or electromagnet is usually stationary, and a steel drum or belt rotates past the magnet, so that magnetic metals are diverted from the waste stream.

In this form, magnetic separation is appropriate only for the highly ferromagnetic materials (iron, nickel, and most ferrous alloys) but recently the "*high gradient magnetic separation*" (HGMS) technique has been reported to be nearing marked breakthrough. HGMS devices, which involve canisters packed with finely divided ferromagnetic material (such as stainless steel wool) in a magnetic field, are able to separate even very small and weakly magnetic (e.g. paramagnetic) particles from a liquid slurry. High magnetic field gradients are created along the filament edges, trapping magnetic particles. To recover the magnetic

material the magnetic field is turned off and the material is flushed out.

Electromagnetic methods are not limited to ferromagnetic articles. Devices utilizing the induction of *eddy currents* (the electrical currents which flow in any conductor when the electromagnetic field through it is changing) may be used to separate non-ferrous metals from non conducting (non-metallic) materials, in urban waste for example, as the mixed waste is fed over the cylindrical separator the magnetic field associated with the eddy currents induced in the metals causes them to be attracted and held for separation. The density of the conductor and its ability to sustain an eddy current flow and so generate its own magnetic field are the basis of the selection properties. They can be expressed in terms of the ratio of electrical conductivity to density.

In the so-called "aluminium magnet" a poly-phase, alternating electromagnetic field sweeps the aluminium (which has a conductivity/density ratio much higher than that of other metals commonly present in waste) laterally off a moving belt. These devices are still largely in the development and prototype stage.

The direct measurement of *electrical conductivity* may be utilized: one or more of a series of electrical probes maintained at a steady potential with respect to an earthing conductor makes contact with each item, and the current through the article codes it on the basis of conductivity and permits it to be diverted by an air blast or similar sorting device.

Electrostatic precipitation is based on the fact that a charged particle placed in an electric field will move towards the electrode of polarity opposite to that on the particle. It is widely used to extract grit and dust from gases, particularly from incineration combustion gases. High voltage direct current is applied between the discharge or ionizing wires (negative) and collecting plates (positive). The ionized gas molecules so produced move towards the collecting plates, colliding with dust particles which thereby become negatively charged and move towards and adhere to the collecting plates. Electrostatic separators can also be used for the removal of plastic from other material: as the mixed waste is fed on to an earthed drum rotating in a high electric field gradient, the plastic is held on the drum and removed by a fixed blade. The technique can also be used for separation of conductors such as aluminium from non-conductors in mixed solid waste.

Electromagnetic radiation ranging from microwave, through infrared, visible, ultraviolet, X-rays and emission from radioactive sources, is potentially available for coding and separating items of waste material, and all are being investigated. The simplest technique is probably the optical scanner, using a broad band of *visible radiation* to separate optically transparent from opaque materials: for example glass from aluminium, as they have nearly identical densities (2.7g cm^{-3}) and are difficult to separate on this basis. Bottles or glass fragments can be sorted into green, amber and clear as they fall from the end of a belt by three photocells which compare the colour of the glass to a reference background colour, and operate rapid-acting air blasts to divert each piece appropriately. Reflected light can also be used.

The spectrum of *infrared radiation* diffusely reflected from a surface shows all the major infrared absorption lines characteristic of the reflector. Infrared radiation is superior to visible light for many

sorting purposes because it is not misled by superficial coloured dyes or inks, and because it can be used in normal room light. Reflection is more convenient than transmission in practical situations, and diffuse spectra from "dull" reflectors are more informative than specular (mirror) reflection from "shiny" surfaces. In the sorting of a limited range of items, one wavelength is adequate, but in the Massachusetts Institute of Technology automated urban waste sorting system mentioned above, a sensor measures the diffusely reflected light intensity at four infrared wavelengths produced in turn by a rotating filter wheel. Careful selection of these wavelengths allows the relative intensities to be made extremely sensitive to the reflecting material. The four peak heights are measured electronically and computer-processed.

A proposed extension of the spectroscopic method is a device in which a high-power pulsed laser or a spark beam vaporizes a very small portion of an object, the vapour then being rapidly analyzed in a manner similar to the widely used flame photometry technique. In principle this method could provide adequate information for precise classification of waste items.

It has even been suggested, in connection with recycling poly(tetrafluorethylene), that a high energy laser beam could vaporize small, dark, light-absorbing objects to remove them completely from light coloured objects which would reflect rather than absorb the radiation.

Filtration and screening are obvious techniques for the separation of solids from liquids and gases, or size-separating solids, with the filters or screens chosen for the particular application and an appropriate pressure drop between inlet and outlet of the filter. The usual distinction between "screens" and "filters" is that the former generally contain regular holes of relatively large size and operate at low pressure drops, while the latter usually have irregular-shaped holes of relatively small size (e.g. a fibrous sheet) and operate at relatively high pressure differentials.

Cellulose fibres can be screened from hydropulped urban waste, and even dry screening can remove a large proportion of the dirt from many materials. Dissolved solids are occasionally removed by evaporation of the solvent, but the value of the recovered residue must outweigh the fuel cost. Evaporation is more commonly used to concentrate a solution and so facilitate subsequent crystallization and filtration. If a dissolved material can be induced to crystallize from a filtered solution it can usually be recovered in a particularly pure form, although the method is expensive if dilute solutions must first be concentrated by evaporation.

Filtration rate of fine solids from liquids is often a problem, with sludge particles plugging the filter pores. Also, sedimentation tanks may be used to allow settling (and aging or recrystallization in the case of crystalline solids), and flocculation tanks in which chemicals are added to improve the separation of colloidal solids, may be incorporated. Elutriation (washing the solids) can reduce the amount of coagulant required. Addition of fly ash (from incinerators or power stations) substantially improves the settling characteristics of slurries in some cases (and thus two waste problems partially cancel each other).

Dust can be removed from gas streams by a fibrous or laminar filter material such as cotton, wool, synthetic fibre, wire wool, or paper, which may be used dry or wetted with a suitable liquid. Particles ranging from $0.01\mu\text{m}$

to coarse screen sizes may be successfully filtered at better than 99% efficiency.

The direct application of density differences (the *sink-float* approach) may involve a single liquid, but often relies on the use of several liquids differing in composition and therefore in density. For example, experimental work has been carried out on the separation of three types of plastic waste using only water. The mixed plastics are fed into a sink-float separator that floated off the polyolefins (polypropylene and polyethylene); the other two components, after sinking, are transported by airlift or an air elutriation column which separates poly (vinyl chloride) from polystyrene.

For high value heavy metals more costly liquids such as tetrabromoethane-methylene iodide and thallium formate/thallium malonate may be used. Alternatively, water slurries of finely-ground, inert materials such as magnetite, ferrosilicon, or galena can be used to provide slurry densities up to 4 g cm^{-3} .

Water classification, elutriation, or rising current separation utilizes an upward-flowing water current to carry lighter particles while denser materials fall back through the column. Water classification and sink-float with water-galena slurries gave comparable results in separating non-ferrous metals from non-metals in automobile shredder rejects.

The beneficiation processes just described are gravitational methods; more efficient are the devices utilizing other forces. Centrifuges produce a force by acceleration of the feed, and in cyclones the force is applied by introducing the pressurized stream tangentially to an inverted cone. Thus dirt, glass and metal objects can be separated from an organic slurry in urban waste treatment. A combination of gravitational and viscous drag is utilized in a vortex classifier: water is used as the medium for separating inorganic materials, while air is suitable for the less dense organic materials. In the inward-flowing air vortex the material is distributed in a continuous manner over a range of density-drag combinations which characterize different objects.

In the *froth flotation* process a gas (usually air) is pumped through a liquid, and the bubbles attach themselves to solid particles, buoying them up the surface. The bubbles are usually negatively charged because the anions (negative ions) collect mainly on the air side of the air-water interface while the cations (positive ions) are distributed in the water on the other side of the interface. Suspended particles with positive charges may be attracted to bubbles; alternatively bubbles can be trapped in the floc structure. As well as its application to inorganic materials like metal oxides from incinerator residue, froth flotation can be used for the separation of water-insoluble fats and precipitated protein, as in the treatment of slaughter house and poultry-packing waters.

Winnowing, *air elutriation*, or *air classification* is useful for the separation of materials of different density but of similar particle size. Examples are the separation of paper labels from crushed glass, differentiation of plastic waste, and resource recovery from urban waste. It works on the principle that objects with a combination of low density and high drag (air resistance) are entrained into a rising air stream, while heavier or

lower drag pieces descend.

A rather different type of air separation process is the *fluidized bed*: low pressure air entering through the porous base of an inclined bed of particles causes them to act as a fluid, with effective densities ranging from less than that of water (1 g cm^{-3}) to more than 4 g cm^{-3} . The less-dense material "floats" on the fluidized bed, while the denser material sinks. The separation of non-ferrous incinerator clinker into light (aluminium-rich) and heavy (copper-rich fractions) has been carried out on a fluidized bed of ferrosilicon, magnetite, or iron particles, the density of the medium being chosen to lie between the densities of the materials to be separated. Aluminium and copper from shredded car radiators can be separated cleanly in the same way. An extension of the method utilizes the *direct* air-fluidization of the dry materials to be processed: this has been called a pneumatic pinched sluice. Low pressure air is admitted to the airbox, and the dry material to be sorted is fed to the wide end of the sluice. During the fluidized flow, the heavier particles sink, and move at lower velocity because of frictional contact with the deck surface. The lighter layers move more rapidly and follow different discharge flight paths.

A very effective way of separating materials is to *selectively dissolve* or *solvent extract* one of them into a liquid phase, leaving the remainder in the solid or gas phases. In principle any mixture of gases, liquids or solids can be separated into its components with the aid of one or more solvents under certain conditions of temperature and pressure, but in practice there are several problems. Selectivity between gases is not usually good unless a chemical reaction removes one gas, as in the reaction of carbon dioxide with limewater to precipitate calcium carbonate, for example. Ionic solids (salts) tend to dissolve in water and other "ionizing" solvents, while covalent materials (the majority of organic compounds) have a greater solubility in organic solvents like hydrocarbons, acetone, and carbon tetrachloride. Metals must normally be converted into their ionic form, by reaction with acid for example, before solvent separation methods can be used. Many metal ions are soluble in water but the use of non-aqueous solvents allows selective dissolution of some metals for example copper in acetonitrile.

Unless water is a suitable solvent, solvent extraction methods involve the expense of a solvent, not all of which is recovered in each cycle, as well as considerable chemical engineering resources. Consequently, they are not extensively used at present in recycling, although this situation will change as the necessity for the recycling of certain materials becomes greater, waste water effluent content becomes more tightly controlled, and the extra cost becomes relatively more acceptable. Applications include the recovery of nickel and cobalt from scrap, of metals and acids from stainless steel pickling (cleaning) solutions, and of zinc from the drainage water in rayon manufacture.

Work is in progress into determining suitable solvents for separation or extraction of polymers. For example, polystyrene dissolves in *p*-xylene, and after filtration it can be precipitated as a pure powder by the addition of methanol. Polythene can also be recovered with xylene as a solvent. A common solvent (eg. 15% cyclohexanone, 85% xylene) for polystyrene, poly(vinyl chloride) and the polyolefins has been found which results in the formation of three phases at 115-125°C, with one polymer type predominating in each phase. At 15% total polymer, the

separated polymers appear to be above 99% pure.

Hard materials are often separated from soft ones by dropping the mixture on to a moving belt: the hard items bounce off, the soft ones remain. This can be used to separate glass from compost manufactured from urban waste. A much more precise use of this characteristic property of materials is the impact sensor.

In the Massachusetts Institute of Technology prototype urban waste separation system, items are struck by a tool on which an accelerometer is mounted, and the deceleration of the tool depends on the material. This information can be computer-analyzed to assist in the coding process.

The difference in frictional resistance between various components of a mixture and a striker/slider plate can be utilized to separate metallic from non-metallic items.

A simple type of ballistic or inertial separator has been devised based on the fact that dense objects leaving a feeding conveyor are projected further than less dense ones, and this may be assisted by the winnowing action of an air stream.

Molecular Separation

All the processes described so far involve the separation of materials in macroscopic amounts; each particle transferred or separated is large compared with the molecular scale. However, it is also possible to conduct separations at the molecular level, with adsorption, membrane processes (dialysis, electrodialysis, reverse osmosis, ultra filtration), and ion exchange and electrodeposition. These have the advantage of usually yielding purer products than phase separation and density difference methods.

Filter aids such as diatomaceous earth (a mineral composed of fossilized silica skeletons of microscopic water creatures), fibrous asbestos, and cellulose are used to remove suspended solids at high filtration rates, but they do not have strong adsorption properties. They depend for their action on the formation of a porous cake which traps suspended matter in small flow channels.

Active or adsorbent materials with high surface areas, notably activated charcoal, coke, and alumina, in slurries, packed beds or fluidized beds are used to adsorb a variety of soluble organic compounds from liquid and gaseous waste streams. This adsorbed material can be recovered by thermal or electrochemical "reactivation" of the adsorbent.

Active carbons are manufactured from carbon-rich material by controlled heating to obtain a carbonized solid product which is then treated with steam or oxidizing gases to develop the internal pore structure. It is also possible to make active filter aids capable of removing both insoluble suspended solids and some soluble impurities. Materials can be prepared which are suitable for a range of filter aid and adsorption applications from coal and cellulosic wastes such as wood, textiles and nut shells.

Synthetic adsorbents (polymeric, porous, spherical beads with controlled surface polarities, surface areas and pore sizes) are now available to facilitate the recovery of organic materials from wastewater. Sometimes simple and inexpensive adsorption media may be used: thus the concentration of ionic constituents of sewage can be reduced in sand filters or by treatment involving lime and rubber derived from discarded tyres.

In *membrane processes*, an appropriate driving force (concentration, voltage, or pressure) causes a flow of a component of a mixed waste stream through a membrane.

Dialysis employs concentration differences as the driving force to separate solutes by means of their unequal diffusion rates through membranes. The energy required to partially separate the components in the mixture is provided by the dilution of the diffusate and dialyzate. Separations are made on the basis of either molecular size or of diffusion rates of solvent and solute; it is usually used to separate solute molecules (which pass through a membrane) from colloidal particles which are retained by the membrane. The related technique of *electrodialysis* uses electromotive driving force, with membranes able to selectively pass either cations or anions: the membrane contains positive or negative ionic charges, and so acts as an electric charge filter.

Ultrafiltration and *reverse osmosis* methods both use pressure to force a solution through permeable and semipermeable membranes, which are now becoming available in a variety of materials and designs suitable for various purposes. In *ultrafiltration* the waste stream is pumped through a porous tube on which a membrane or colloidal gel has been cast. The hydraulic pressure causes water and some dissolved low molecular mass materials to pass through the small pores, but emulsified oils or suspended protein particles are retained and concentrated within the tube. Gels or membranes to carry out this process are sometimes called *molecular sieves*.

Reverse osmosis is the use of a pressure gradient to cause only the solvent to pass through a semipermeable membrane, thus concentrating the solutes and purifying the solvent. A thin (usually less than 0.1 μm), dense, semipermeable skin of cellulose acetate (or more recently other synthetic polymers) is uniformly deposited and firmly anchored to a thicker (about 20 μm), strong and tough porous layer supported in some way to prevent rupture. Because reverse osmosis uses surface filtration rather than deep filtration, fouling on the membrane can be readily removed by hydraulic or chemical methods. Several types of reverse osmosis system are now commercially available, each with particular advantages in certain situations. The main applications are in water recycling, including desalination of saline or brackish water, and in conjunction with ultrafiltration to separate protein and lactose from cheese whey and similar "wastes". Wastewater streams containing 1-5% water-emulsified or water-soluble cutting oils can be processed to produce liquids containing 30-60% oil and a permeate with a low chemical oxygen demand. Reverse osmosis has proved satisfactory in the recycling of papermill water, and the removal of pesticides from water.

Thermal separation methods

Selective melting (or "sweating") due to differences in melting points may be utilized to effect separations of metals. A furnace fitted with a sloping hearth may be used to allow collection of the molten fraction, and some provision is usually made to vibrate the melting mixture.

Recently, baths of molten salts have proved superior for this purpose: oxidation is inhibited and cleaner products are obtained. Copper-containing scrap such as generators, alternators and electric motors are dipped in molten calcium chloride and agitated briefly. The copper melts and flows out of even inaccessible crevices to collect at the bottom of the container where it can be tapped off in about 99% yield. The steel scrap is little affected, and the salt can be reused.

The technical feasibility of vaporizing metal impurities from recycled automotive scrap steels by *melting under vacuum* has been evaluated. Copper and tin levels are decreased to acceptable levels, and chromium can be removed if the carbon concentration is first reduced.

Electroslag melting, in which the heating is carried out by the passage of an electric current through a molten salt or slag and impurities are removed from the molten steel by extraction into the slag layer, is successful for the removal of chromium, tin, and aluminium, but not copper.

Distillation involves heating a mixture of compounds in a closed system, so that the components of highest vapour pressure distil off and are deposited as a liquid (or occasionally solid) "distillate" on a cooled surface. Several components can be separated in batch processes by careful temperature control, but recovery of a single solvent is frequently carried out by an in-line, continuous process. In *steam distillation* superheated steam is introduced directly into the mixture, and the distillate contains a mixture of the more volatile components with water. If these are immiscible, separation of the layers occurs automatically, but in the recovery of water-soluble materials *fractionation* is required. This is the separation of liquid mixtures by the use of differences in boiling points and molecular masses. The vapours flow up a column, and by adjusting the heat input, liquids of known content can be removed at various heights in the column. It is a relatively expensive process, justified only for the recovery of more valuable materials. This is also true of *vacuum distillation*, where heat is applied to the system maintained under vacuum to lower boiling point. It is necessary for the recovery of heat-sensitive materials. All the distillation methods are most frequently applied to the recovery of solvents.

Selective cryogenic embrittlement: Rubber tyres cooled to -60°C in liquid nitrogen (boiling point -196°C) can be granulated by a hammer mill and the resulting rubber crumb (as well as fibre fluff and metal beading) used for a variety of purposes such as sports surfaces and carpet underlay, and this is now being done in Perth. The same

cryogenic recycling technique can be applied to cans, plastics and to insulated copper and aluminium wire: after embrittlement, insulation and coatings separate easily from the wire. The important properties here are the ductile-brittle transition temperature of metals and the glass transition temperatures of polymers.

At a temperature of -120°C iron is very much more brittle than aluminium and copper. By pre-cooling mixed metals in liquid nitrogen it is therefore possible to shred ferrous metals into flakes which are much smaller than non-ferrous fragments accompanying them. Baled car bodies and other mixed metal scrap can thus yield a high quality scrap of approximately 99% ferrous material. The technique is particularly suitable for the recovery of copper from small electric motors.

Thermoplastics: Polymeric materials which become soft when heated and can be moulded, extruded, and shaped are called "thermoplastics" (in contrast to the thermosetting or chemically hardened plastics which do not soften on reheating and cannot be remoulded). Thermoplastics, particularly polyethylene, polypropylene, polystyrene and poly (vinyl chloride), comprise nearly three quarters of the total plastics produced. Most of the waste thermoplastic generated within manufacturing processes is recycled, but waste scrap of mixed and unknown properties is usually unacceptable in current processes. There are examples of certain products being manufactured from particular items available in large quantity (high density polyethylene milk bottles being recycled as drainage tiles for example). Other products such as traffic markers, parking barriers and paving blocks where material specifications need not be so precise utilize recovered thermoplastics separated by sink-float and air elutriation techniques.

Drying is one of the everyday applications of heat, and although there are numerous examples of such processes in recycling, only one will be mentioned here, chosen because it illustrates the recycle philosophy applied to a simple yet important system. There has been developed a process for the manufacture of a stock feed ingredient by dehydrating wet cow manure extrusions in a packed bed, using superheated steam as the drying medium in a closed cycle. The closed cycle eliminates odour problems; the superheated steam kills virtually all organisms and is more efficient than air for the purpose because it can be totally recycled whereas air would require a purge stream to control moisture build-up.

Separation by Exchange Reactions

Ion exchange is the reversible exchange of ions between a solid ion exchange resin (usually in the form of beads in a packed column or fluidized bed) and a liquid in which there is no substantial change in the structure of the solid. This technique is particularly suitable for the recovery of ions present in solution at low concentrations, and it is unsuitable for seawater desalination, for example. The resins used were originally inorganic ("zeolites") but now most are three-dimensional organic networks to which are attached many ionizable groups. Hydrogen ions (H^+) on the cationic resin $(\text{RCO}_2)\text{H}$ or $(\text{RSO}_3)\text{H}_2$.

can be replaced by metal ions. The bound metal ion is subsequently released to form a concentrated solution for recovery by the addition of strong acid. Alternatively, one metal ion can replace another.

In this way a pollutant ion may be removed from the waste stream and concentrated for re-use. In Australia a process ("Sirotherm") is being developed to utilize low-grade heat (under 90°C) instead of chemicals to regenerate resins. The special mixed resin absorbs salt at 20°C, but when the temperature is raised to 80°C the position of equilibrium is reversed and a concentrated salt effluent is produced.

Resins are ideal for the concentration and recovery of the more valuable metal ions, particularly from electroplating baths: the noble metals, silver, copper, zinc, nickel, tin (as stannate) and chromium (as chromate) for example.

Uranium is recovered from acid leach mine waters by ion exchange. At the other end of the concentration range, resins may be used for water purification and recycling by removing trace amounts of ions.

Resins may also be used for removing or recovering any organic materials which can be converted to an ionized (charged) form, particularly acids (tartaric, acetic, etc.). They are, however, vulnerable to organic fouling, and pretreatment of many liquors is necessary. Macroporous (large-pored) resins used in some sewage treatment systems have overcome many of these problems.

Although synthetic ion exchange resins are efficient, they are expensive, and alternative cheap or free materials have been suggested for the removal of toxic heavy metal ions from mining and industrial waste streams. Many agricultural and forestry byproducts (peanut skins, walnut expeller meal, wood barks, coconut husks) contain tannin and in laboratory tests have proved to be excellent scavengers for Cu^{2+} (cupric), Hg^{2+} (mercuric) Pb^{2+} (lead), Zn^{2+} (zinc) and Cd^{2+} (cadmium) ions, reducing their concentrations to levels below the usual effluent standards. Each sorbed metal ion (M^{2+}) displaces two hydrogen ions (H^+) so the position of equilibrium is acid dependent and the metals can be recovered in concentrated solution by acid treatment.

When an electrical potential difference is applied between two electrodes in an electrolyte solution materials are deposited or dissolved at different characteristic voltages (called electrode potentials). If the appropriate voltage is used in a suitable electrolyte, it is possible on the one hand to selectively plate out metals or evolve liquids and gases, and on the other to selectively dissolve metals. The collective term for all these processes is *controlled potential electrolysis*. Fluidized bed electrodes provide large electrode surface areas, are proving preferable for dilute solutions.

Metals such as copper, zinc, and aluminium are usually extracted and purified by electrodeposition anyway, so the extension of the process to waste recovery by electrolysis preceded, if necessary, by chemical dissolution has been relatively simple. Thus zinc metal can be recovered from smelter flue dusts, and copper metal can be separated from complex aggregates in the scrap from the electronics industry or from acid pickling wastes. Recovery of copper, nickel and zinc by

electrolysis of effluents has in general reached a high state of efficiency, and electrolysis has been applied also to silver, arsenic, gold, and chromium recovery.

Nickel and cobalt salts have very close standard electrode potentials in aqueous solution, but when they are dissolved in a molten salt such as a mixture of lithium chloride and potassium chloride at several hundred degrees Celsius, nickel can be plated out with less than 0.1% cobalt from starting alloys with up to 5.5% cobalt. After all the nickel has been removed, the voltage can be adjusted and the cobalt plated out.

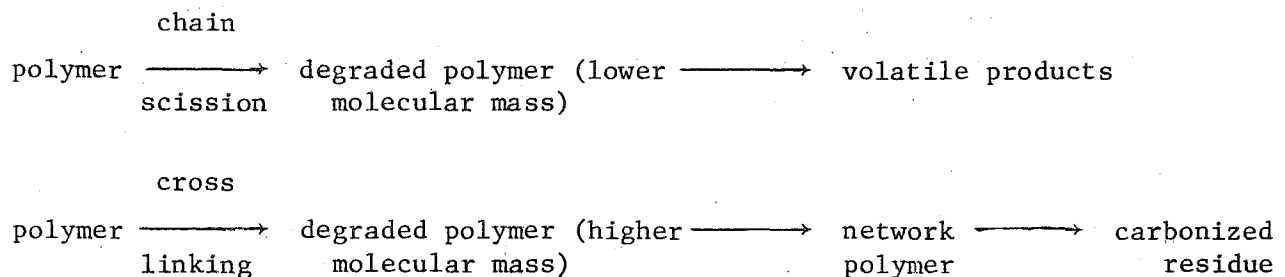
A process which occurs by an electrochemical mechanism but which does not require the application of an electrical potential from an external source is "*cementation*" or *metal displacement*: the precipitation of a metal from solution by the sacrificial dissolution of a less noble metal (i.e. of a metal with a more negative standard electrode reduction potential). These reactions have been used for at least two thousand years as a means of extracting metals from solution, and the oldest process is still applied for the recovery of copper metal by means of scrap iron or other metal. On technical grounds, magnesium and aluminium are preferred, but frequently economics determines that iron is the choice.

Silver metal can be recovered from photographic wastes in a similar way by bringing the waste solutions into contact with turnings of a metal alloy containing aluminium and magnesium.

Chemical vapour transport: If an element forms a suitable volatile compound it is sometimes possible to distil the element from a mixture or alloy and condense it in a pure form. The halogen compounds of titanium (TiCl_4) and aluminium (AlCl_3 and AlCl) are good examples.

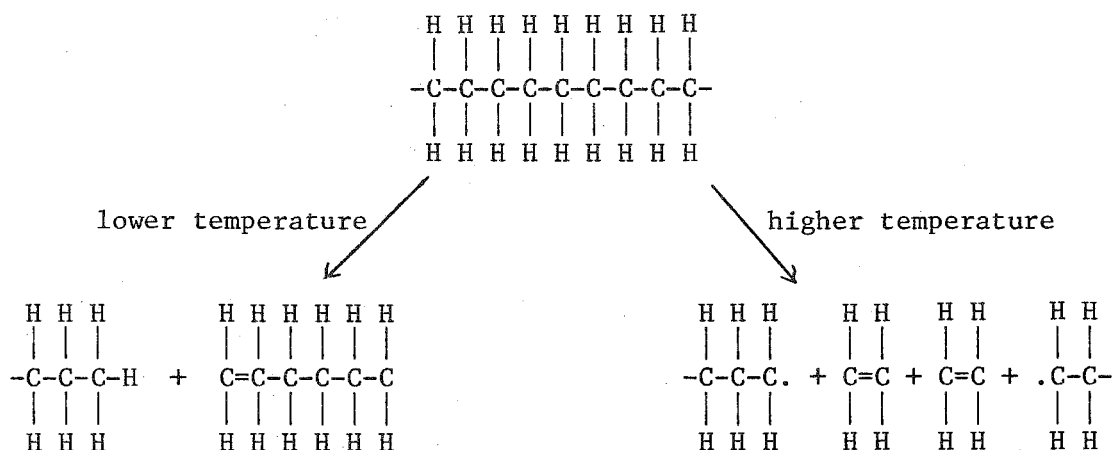
Depolymerization

Thermal degradation of a polymer involves a series of chemical reactions, some of which may be the reverse of the addition polymerization steps and involve *chain scission* with reactive intermediates such as free radicals. An alternative possibility in thermal degradation is *cross-linking*, the formation of chemical bonds between neighbouring chains through side groups. In this case the molecular mass increases, a rigid three-dimensional network forms, and if heating continues eventually carbonization occurs. The two processes may be summarized:



In some cases both processes are important, and are in competition. Oxidation and reduction reactions occurring at higher temperatures, in the presence of adequate, limited or no oxygen and resulting in more fundamental chemical changes are discussed in subsequent sections.

Poly(methyl methacrylate) and poly(methyl styrene) depolymerize to monomer in 100% yield, and poly(tetrafluoroethylene) gives greater than 95% yield of the monomer under the optimum conditions with superheated steam. Other addition polymers, such as polystyrene and polyethylene tend to depolymerize but there are several competing reactions causing cross-linking of chains. The polyethylene chain, for example, does not "unzip" during depolymerization, but is randomly broken and reformed, so the monomer yield at 200°C is only 0.1%. At high temperatures fragmentation is more extensive. The low and high temperature mechanisms can be depicted as follows.



Hydrolysis is a rather general chemical term applied to any reaction of a material with water, frequently in the presence of an alkali or acid, and sometimes at high temperatures and pressures. In the same way that chain scission is the reverse of addition polymerization, the hydrolytic degradation of polymers is formally the reverse of condensation polymerization. The term *solvolysis* extends the scope of "hydrolysis" to solvents other than water, such as alcohols.

The most interesting application of polymer hydrolysis in recycling is the suggestion that cellulose from paper and other organic waste materials can be converted economically into glucose (followed by fermentation to ethanol, for example).

There is also a growing interest in the solvolysis of synthetic polymers. Thus poly(acrylonitrile) wastes hydrolyze to a water-soluble mixture of compounds containing amide and carbonyl groups, and the hydrolysis of poly urethane foam waste with water at 200°C results in 65-80% recovery of solid 2,4- and 2,6- toluene diamines, with a liquid residue consisting of ~ 98% polypropylene oxide. It is probable that these products could be economically utilized.

The study of *photolytic* degradation of polymers (chemical decomposition initiated by light) has been prompted by a desire on the part of a proportion of the public for degradable plastic containers, so that when littered they have relatively short lives and do not accumulate. The principle of the photochemical approach to the degradation of plastics is the application of the fact that window glass acts as a filter to sunlight, preventing the transmission of most of the ultraviolet radiation (radiation with wavelengths shorter than about 320 nm). If it is possible to incorporate chemical groups into polymer chains such that degradation is initiated by light of wavelength less than 320 nm, the containers will degrade only when left outdoors.

Photolytic scission of a carbon-carbon bond is the initial step, leading to the formation of free radicals and further fragmentation (the reverse of addition polymerization). In the presence of oxygen, an oxidative mechanism can continue after the photoinitiation, and subsequently biodegradation of the smaller polymer fragments can complete the process.

There are several other methods of polymer degradation which may prove equally useful in the future, ranging from mastication (which is already applied to rubber reclamation) to various irradiation techniques (which are at present little used).

Thermoplastic polymers can be *re-extruded*, in some cases after degradation by one of the above methods. The process is assisted in some cases by the addition of a small amount of an appropriate solvent. Short fibres can be prepared by solution spinning or melt spinning techniques applied to waste polymers or polymer mixtures, the short fibres being pressed into a fibreboard or paper-like nonwoven sheets. "Graft copolymerization" can be carried out: a catalyst or radiation is used to initiate radical formation on the existing polymer chains, resulting in chain cross-linking or copolymerization with groups exhibiting special properties. Thus wiping cloths could be manufactured by grafting cellulose or starch (to impart water absorptivity) or hydrocarbons (to enhance oil absorptivity) onto compressed fibre polymer sheet.

Incineration

The simplest and most obvious way of recovering some of the values from any organic waste is burning it for its energy content, and this may even be the most efficient utilization of wastes in many cases. It has an initial advantage in that the reagent, oxygen, is available at low cost. Contaminants (such as insecticides in crop wastes) are destroyed. Steam may be produced for heating and/or electricity generation, for desalinating water, and for drying the incoming fuel. Urban waste, for example, compares quite favourably with some coals as a fuel. On a larger scale, it has been suggested that coal refuse piles might be burned to provide both energy and a usable ash.

Problems arise in the incineration of synthetic polymers (plastics) which are not found in the natural carbohydrate polymers: the production of corrosive gases such as hydrogen chloride and chlorine from polyvinyl chloride; the higher thermal output, and the tendency of thermoplastics to clog grates. Recent innovations have included the use of fluidized beds and high temperature molten salt and liquid metal reactors.

Pyrolysis

Pyrolysis or destructive distillation is chemical decomposition of a carbonaceous material by heat (usually 400-900°C) in the absence of oxygen, or in a controlled oxygen environment. The process has been used for hundreds of years, notably to convert coal to coke for the iron-making industry and for town-gas production.

Pyrolysis leads to the formation of three component products in relative amounts which depend on the pyrolysis conditions:

- (a) a *gas* component including such low relative molecular mass compounds as hydrogen, methane, carbon monoxide and carbon dioxide;
- (b) an *oil*, including compounds such as acetic acid, acetone, methanol and furfural, with relative molecular masses in general lower than those in the starting material; and
- (c) a *char*, containing carbon and any inert inorganics that were present. There is also an aqueous mixture.

In general, the more rapid the decomposition (high temperature, high heating rate) the higher the yield of gas; a long, slow heating process results in a higher proportion of oil and char. The mechanism of this process is complex, but a start can be made to understanding it by studying the thermal decomposition of cellulose.

On rapid heating in the absence of oxygen the cellulose molecule "explodes", and the fragments form many simple compounds, including methane, carbon dioxide, hydrogen, carbon monoxide and water. At lower heating rates the molecules have sufficient time to reorganize into more thermally stable liquids, and eventually solids that become increasingly hard to break down.

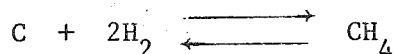
The key factor in producing a high energy pyrolysis gas (without additional hydrogenation, which is expensive), is a high hydrogen/carbon ratio in the fuel.

Based on their potential to produce hydrogen, the solid wastes are superior to the solid fuels in current use, and in fact have H/C ratios comparable to those of liquid hydrocarbons. Pyrolysis has been applied to a variety of organic waste materials including wood bark plastics, sawdust, scrap tyres, urban waste and plant waste. Pyrolysis is particularly applicable to rubber tyres: one old tyre can produce approximately enough carbon black for one new tyre as well as oil and gas.

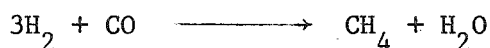
Other Upgraded Fuels

A common method of reduction of organic material is direct reaction with hydrogen in the presence of a catalyst at high enough temperatures (500-700°C) and pressures (7-18 MPa, 1000-2700 p.s.i.) to produce methane.

Carbon monoxide produced during the organic decomposition can be "shifted" to carbon dioxide and hydrogen, and the carbon dioxide scrubbed out or removed by "methanation":



water gas "shift"



methanation

to yield a "substitute natural gas" (SNG) containing mainly hydrogen, methane, and ethane, and suitable for pipeline distribution, gas turbine operation, or (with a high hydrogen content) in hydrogen fuel cells.

Cellulosic material is greatly improved as a fuel if it is treated in such a way that a low oxygen content liquid product is obtained, with the oxygen being removed as carbon dioxide (decarboxylation) rather than as water (dehydration) so that the hydrogen/carbon mole ratio remains high.

The reduction of carbonaceous material in a water or oil slurry with steam and carbon monoxide produces a high calorific value heavy fuel oil with a typical empirical formula $\text{C}_{6.6}\text{H}_{6.5}\text{O}_{0.5}$. The reaction occurs at temperatures (250–400°C) significantly lower than those necessary for hydrogasification, but at rather high pressures because of the steam pressure.

As in the hydrogasification process, the carbon monoxide may be produced from organic materials in another reactor, and need not be pure: synthesis gas, a mixture of carbon monoxide and hydrogen, is satisfactory. An alkaline catalyst such as sodium carbonate or bicarbonate is necessary, although at higher temperatures the natural alkalinity of some organic waste is adequate.

If carbonaceous material is introduced at the top of a fixed bed reactor, and some oxygen-containing gas (air, oxygen, steam) is introduced at the bottom, the organic material progressively undergoes the following processes as it moves down:

- (i) drying
- (ii) first stage decomposition, driving off water, carbon dioxide and carbon monoxide
- (iii) tar formation
- (iv) char formation, with evolution of hydrogen, methane, and ethane

- (v) char oxidation by the introduced oxygen or steam, or by carbon dioxide

This, in effect, combines the two processes of pyrolysis and hydrogasification in the one reactor. Heat transfer and gas transport rates in the pyrolysis process are essentially the same as those which occur in an externally heated vessel under a slow heating rate.

The temperature reached may be high enough to melt any inorganic residue, and this feature is utilized in some high temperature incineration systems. The output gas can be upgraded to a substitute natural gas (particularly if oxygen rather than air is used as oxidant) and used in the same way as the hydrogasification product, above.

The hydrogen derived from a pyrolysis or partial oxidation plus water gas shift can be utilized as a chemical rather than directly as a fuel. The energy of waste materials is thus converted indirectly into a fuel such as methanol or a fertilizer such as ammonia by catalytic synthesis.

Reactors

Many thermal solid-gas reaction processes are carried out in *fixed-bed* reactors, either batch or continuous. In the case of continuous processes, which are becoming more popular, the fuel enters from the top and moves slowly down a vertical shaft or inclined bed through the reaction zones while air or oxidizing gas and hot reaction products move upwards.

Rotary kiln reactors overcome problems of fixed bed reactors which arise through channeling and uneven reaction, but are more expensive. *Fluidized beds* can be used in reaction processes, including high temperature oxidation-reduction. The beds are normally pre-heated by burning a gaseous fuel before the finely-divided solid is introduced. Fluidized bed incineration is one form of *suspension firing*. Another approach, *vortex incineration* burns the fuel as it is blown tangentially into the combustion chamber, reducing residence time and improving efficiency.

An alternative high temperature suspension "fluid" is a liquid: thus a *molten metal*, lead, has been used for pyrolysis. More commonly an *ionic liquid* (molten salt) is used, for example various mixtures of alkali halides and alkali nitrates for the oxidation of wastes and surface coatings and for the electrorecovery of nickel and cobalt from their alloys. In the former cases it is believed that a reactive oxidizing agent is present in small, equilibrium quantities in the melt; in the latter case the molten salt is simply acting as a highly conducting, mobil, electrolytic liquid.

Hydrometallurgy and pyrometallurgy

In *hydrometallurgy*, which is widely used in the processing of copper and nickel ores for example, but which can be applied equally well to many wastes, the materials are dissolved in a suitable solvent and then

separated by a variety of chemically-based operations. The solvent is often water, but recent developments use organic solvents such as acetonitrile. The usual recovery scheme for metals is acid dissolution, separation of metal ions from solution, and recovery as metals, oxides, or salts as appropriate. The method can be applied to complex alloy scraps such as bearings, electrochemical machining sludges, and metal production and finishing wastes.

Pyrometallurgy (extraction of materials by a process requiring the application of heat) is a well established method of obtaining metals from ores, and in some fields is highly developed technologically, even if the scientific bases of the methods are not always fully elucidated.

In some cases only minor modifications are necessary for pyrometallurgy to process waste materials from other industries or to more fully utilize its own "wastes". Particular areas where progress is being made are electric furnace steel-making and foundry pig iron manufacture from cans and from automobile and large appliance scrap; and carbothermic reduction (heating with coke) of copper smelting slags to recover copper, tin, nickel, zinc and iron.